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Nanostructured Fibre Composites, and Materials for Air Filtration



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Abstract

Electrospinning is a method that can be used in the production of polymeric nanofibres. Polymer solution is drawn into nanosized fibres utilizing electric field. In addition to neat polymers, solutions containing additives and fillers can also be used to functionalize fibres for use in specific applications. In addition, the nanosized structure of electrospun fibre web has intrinsic properties which are suitable for various applications. The small fibre diameter, small pore size, and high surface area of the nanofibre web are properties that are advantageous for filtration applications. Electrospun nanofibres can be used as an effective layer in composite filter media.

This thesis studies the preparation of nanostructured fibre composites using the electrospinning method and using of such composites in air filtration applications. The formation of nanofibres using the electrospinning method was examined with neat and composite solutions; the preparation of composite materials containing nanofibre layer was investigated with modelling and in practice; and the use of composite materials in air filtration applications were explored. It was shown that the small fibre diameters that enable the slip-flow effect advantageous for filtration are easily achievable with the electrospinning method. The composite material was used in fibres to obtain intriguing properties, such as porosity throughout the fibre or photo catalytic activity. In some cases the use of composite solutions affected the fibre formation of the electrospinning process compared to neat polymeric solution.

Electrospun nanofibre layers had limited strength so they were produced onto substrates as an effective filtration layer. The preparation of such a layer can be accomplished with multi-nozzle electrospinning equipment as described within this thesis. The modelling of the electric field revealed that while the voltage affected the strength of the field, the overall nature and shape of the field was mainly dependent on the distance between the nozzles and the collector. The filtration efficiency of fibrous substrate clearly increased even with a very low amount of nanofibres, and efficiencies above 99 % were achieved with higher coating weights depending on the particle sizes used in the tests. Increasing the coating weight above 0.5 g/m^2 showed no benefits, and instead raised the pressure drop to an unusable range.

Keywords

Electrospinning, Nanofibre composites, Nanofibre coating, Air filtration

Preface

This work was carried out in the Department of Materials Science at Tampere University of Technology during the years 2003-2008. The reported results were obtained and the knowledge accumulated during several projects as well as in research undertaken outside specific projects. The projects include jointly financed research projects POTRA “*Self-organized functional materials*”, KEPPI “*Field Driven Coating with Polymer Composites*”, and MARAPOKE “*Advanced Material Solutions for PEM Fuel Cells*”, and commissioned research projects NAFI and NAFI2 “*Nano Filter*”. The projects were funded by the National Technology Agency of Finland (TEKES) and Finnish industry.

I first wish to express my gratitude to my supervisor Ali Harlin for his guidance, support, and patience. I am also grateful to all my co-authors from Tampere University of Technology, Helsinki University of Technology, and VTT. I would also like to thank Professor Pertti Nousiainen and all the personnel of Fibre Materials Science for their discussions, valuable comments, support, and practical help during the research work. I am especially indebted to Marja Rissanen and Marju Ferenets for their help and critical reading of the articles and thesis, and to Riitta Salonen for her support and encouragement. I would also like to thank Alan Thompson for revising the English language of the thesis.

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Tampere, 25.8.2008

Pirjo Heikkilä

List of Publications

This thesis is based on following six publications, presented as Papers I to VI.

- I. Ruotsalainen T., Turku J., Heikkilä P., Ruokolainen J., Nykänen A., Laitinen T., Torkkeli M., Serimaa R., ten Brinke G., Harlin A., Ikkala O., Towards internal structuring: Electrospun nanofibers by self-assembly of polymeric comb-shaped supramolecules, *Advanced Materials*, 17(8)2005, 1048-1052
- II. Ristolainen N., Heikkilä P., Harlin A., Seppälä J., Polyvinyl alcohol and polyamide-66 nanocomposites prepared by electrospinning, *Macromolecular Materials and Engineering*, 291(2)2006, 114-122
- III. Heikkilä P., Sipilä A., Peltola M., Taipale A., Harlin A., Electrospun PA coating on textile surfaces, *Textile Research Journal*, 77(11)2007, 864-870
- IV. Heikkilä P., Uusimäki J., Söderlund L., Kettunen L., Harlin A., Exploitation of electric field in controlling of nanofibre spinning process, *Polymer Engineering and Science*, 47(12)2007, 2065-2074
- V. Heikkilä P., Taipale A., Lehtimäki M., Harlin A., Electrospinning of polyamides with different chain compositions for filtration application, *Polymer Engineering and Science*, 48(6)2008, 1168-1176
- VI. Heikkilä P., Harlin A., Parameter study of electrospinning of polyamide-6, *European Polymer Journal*, accepted 23 June 2008, doi:10.1016/j.eurpolymj.2008.06.032

Other publications in the research area, which are not included in the thesis

- Heikkilä P., Pääkkö M., Harlin A., Electrostatic spinning of submicron fibres of synthetic polymers and polymer blends, 4th World Textile Conference AUTEX 2004, 22-24 June 2004, Roubaix, France, 6 p.
- Heikkilä P., Pääkkö M., Harlin A., Electrostatic coating with conducting polymer blend fibre, International Textile Congress, 18-19 Oct. 2004, Terressa, Spain, 8 p.
- Harlin A., Ikkala O., Kosonen H., Valkama S., Ruotsalainen T., Mäki-Ontto R., Turku J., Ruokolainen J., Heikkilä P., A method for manufacturing a fibrous structure, a method for manufacturing a fiber and a fibrous structure, Patent Application WO 2005/049707, 2005
- Harlin A., Heikkilä P., Sipilä A., Ristolainen N., Ruotsalainen T., Novel electrospun fibre structures of the coated aerosol protection textiles, 5th World Textile Conference AUTEX 2005, 27-29 June 2005, Portoroz, Slovenia, 550-557
- Heikkilä P., Harlin A., Söderlund L., Uusimäki J., Kettunen L., Modelling of the electric field of electrospinning process, 7th World Textile Conference AUTEX 2007, 26-28 June 2007, Tampere, Finland, 8 p.
- Heikkilä P., Harlin A., Taipale A., Filtration efficiency of electrospun nanofibres, 7th World Textile Conference AUTEX 2007, 26-28 June 2007, Tampere, Finland, 5 p.
- Heikkilä P., Harlin A., Halmu K. Electrospun nanofibres containing TiO₂, 7th World Textile Conference AUTEX 2007, 26-28 June 2007, Tampere, Finland, 8 p.
- Martikainen L., Heikkilä P., Setälä H., Harlin A., Acid-base controlled electrospinning of polyelectrolyte solution, 7th World Textile Conference AUTEX 2007, 26-28 June 2007, Tampere, Finland, 8 p.
- Ristolainen N., Heikkilä P., Harlin A., Seppälä J., Electrospun nanofibers prepared by two methods: *in situ* emulsion polymerized PVA/nanoTiO₂ and mixing of functional-PVA with nanoTiO₂, *Autex Research Journal*, 8(2)2008, 35-40
- Heikkilä P., Harlin A., Electrospun nanofibres containing carbon nanotubes, 8th World Textile Conference AUTEX 2008, 24-26 June 2008, Biella, Italy, 6 p.

Author's Contribution

Paper I, *"Towards internal structuring: Electrospun nanofibers by self-assembly of polymeric comb-shaped supramolecules"* examines the preparation of electrospun nanofibre with internal nanostructure obtained using self-organizing polymers. The author sketched the conceptual design of the electrospinning equipment used in the experiments, participated in the execution of the experimental part, and participated in the writing of the part of the manuscript dealing with the electrospinning method.

Paper II, *"Polyvinyl alcohol and polyamide-66 nanocomposites prepared by electrospinning"* studies preparation of electrospun composite fibres containing nano-sized clay particles. The author participated in the planning of the experimental part, sketched the conceptual design of the electrospinning equipment used in the experiments, and participated in the execution of the experimental part and the writing of the manuscript.

Paper III, *"Electrospun PA coating on textile surfaces"* examines the preparation of electrospun fibre coating onto textile surfaces and the use of these structures in filtration. The author designed the experimental plan, sketched the conceptual design of the electrospinning equipment used in the experiments, executed the experimental part, participated in the testing of the samples, executed the SEM imaging, and analysed the results. The manuscript was written by the author (except the description of the filtration efficiency measurement system) and commented on by the co-authors.

Paper IV, *"Exploitation of electric field in controlling of nanofibre spinning process"* describes the modelling of the electrospinning process. The author designed the experimental plan, sketched the conceptual design of the electrospinning equipment used in the experiments, and executed the experimental part. The author also took part in the planning of the model, executed the SEM imaging, analysed the results of the electrospinning trials and participated in the analysis of the models. The manuscript was written by the author and commented on by the co-authors.

Paper V, *"Electrospinning of polyamides with different chain compositions for filtration application"* presents results of several electrospinning studies made with different polyamides. The author designed the experimental plan, sketched the conceptual design of the electrospinning equipment used in the experiments, executed the experimental part, participated in the testing of the samples, executed the SEM imaging, and analysed the results. The manuscript was written by author (except the description of filtration efficiency measurement system) and commented on by the co-authors.

Paper VI, *"Parameter study of electrospinning of polyamide-6"* studies the effects of solution and process parameters on the properties of the electrospun fibres and the electrospinning process. The author designed the experimental plan, sketched the conceptual design of the electrospinning equipment used in the experiments, executed the experimental part, participated in the testing of the samples, executed the SEM imaging, and analysed the results. The manuscript was written by the author and commented on by the co-author.

Lists of Symbols and Abbreviations

Symbols

ε	Permittivity
σ	Surface charge
τ	Relaxation time
χ	(Chi) parameter, Flory's χ parameter or Flory-Huggins χ parameter
C	Concentration
C^*	Overlap concentration, limit between dilute and semidilute regime
C^{**}	Limit between semidilute and concentrated regime
C_e	Entanglement concentration, divides semidilute regime into unentangled and entangled sub-regimes
E	Overall strength of the electric field
E_x	x-directional component of the electric field, directed away from the centreline
E_y	y-directional component of the electric field
E_z	z-directional component of the electric field, directed parallel to the centreline
M_n	Number average molecular weight
M_w	Weight average molecular weight
R_g	Radius of gyration
V	Voltage

Abbreviations

AC	Alternating current
AFM	Atomic force microscopy
CA	Cellulose acetate
CNF	Carbon nanofibre
CNT	Carbon nanotube
CVD	Chemical vapour deposition
DC	Direct current
EFCF	Electric field concentration factor
EHD	Electrohydrodynamic spray, electrospray
eSp2	One-nozzle electrospinning equipment for stationary samples at TUT
eSp3	Continuous electrospinning equipment with multiple nozzles at TUT
FEM	Finite element method
FP	Filter of Petryanov, commercial electrospun filter product developed in Soviet Union
HEPA	High efficiency particulate air (filter), according to EN 1822 the collection efficiencies for the MPPS of the HEPA filters are 85 % - 99.995 % (classes H10-H14)
HFP	Hexafluoropropanol
HUT	Helsinki University of Technology
MMA	Methyl metacrylate
MMT	Montmorillonite, clay

MPPS	Most penetrating particle size, typically in the range of 100 nm to 500 nm
MWNT	Multi-walled carbon nanotubes
NFES	Near field electrospinning
NMR	Nuclear magnetic resonance
PA	Polyamide
PAA	Polyacrylic acid
PAN	Polyacrylo nitrile
PANi	Polyaniline
PBI	Polybenzimidazole
PC	Polycarbonate
PE	Polyethylene
PEG	Polyethylene glycole
PEO	Polyethylene oxide
PCL	Poly- ϵ -caprolactone
PDI	Poly dispersity index
PDP	3-n-pentadecylphenol
PLA	Polylactic acid
PLLA	Poly-L-lactide
PCM	Phase change material
PMMA	Polymethyl metacrylate
PP	Polypropylene
PPy	Polypyrrole
PS	Polystyrene
PS- <i>b</i> -P4VP	Polystyrene- <i>block</i> -poly-4-vinylpyridine
PTFE	Polytetrafluoro ethylene
PU	Polyurethane
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
PVP	Polyvinyl pyrrolidone
RT	Room temperature
SAXS	Small angle X-ray scattering
SEM	Scanning electron microscopy
SWNT	Single-walled carbon nanotubes
TEM	Transmission electron microscopy
TUFT	Tubes by fibre template
TUT	Tampere University of Technology
ULPA	Ultra low penetration air (filter), according to EN 1822 the collection efficiencies for the MPPS of the ULPA filters are 99.9995 % - 99.999995 % (classes U15-U17)
VTT	Technical Research Centre of Finland

Table of Contents

Abstract	i
Keywords.....	i
Preface.....	ii
List of Publications.....	iii
Author's Contribution	v
Lists of Symbols and Abbreviations	vi
Table of Contents	viii
1 Introduction.....	1
1.1 Objectives and Approach	4
1.2 Structure of the Thesis	5
2 Electrospinning Method	6
2.1 Polymer Solution	8
2.2 Formation and Instabilities of the Jet	11
2.3 Properties of Electrospun Fibres.....	16
2.4 Electrospinning Designs.....	19
2.5 Models of the Electrospinning Process	23
3 Nanostructured Fibre Composites	26
3.1 Polymeric Blends and Co-Polymers.....	27
3.2 Composite Fibres using Nanofillers	30
3.2.1 Composites with Lamellar Nanoparticles	30
3.2.2 Composites with Nanotubes	32
3.2.3 Composites with Spherical Nanoparticles.....	33
4 Material for Filtration Application.....	35
4.1 Preparation of Nanofibre Web with Multi-Nozzle Electrospinning	35
4.2 Electrospun Fibres in Filtration Applications	37
5 Experimental	44
5.1 Materials.....	44
5.2 Electrospinning.....	45
5.3 Methods of Analysis	46
5.3.1 Filtration Measurements.....	46
5.3.2 Modelling.....	47
6 Preparation of Nanostructured Fibre Composites.....	49
6.1 Neat Polymers.....	49
6.2 Self-Organizing Polymers.....	51
6.3 Fillers in Electrospun Fibres.....	52

7	Formation of Nanofibre Composite Layer	55
7.1	<i>Modelling of Electrospinning</i>	55
7.2	<i>Electrospinning with Multiple Nozzles</i>	58
7.3	<i>Production Rate per Nozzle</i>	60
8	Nanofibre Composite in Filtration	63
8.1	<i>Properties of the Fibrous Web</i>	63
8.2	<i>Filtration Efficiency</i>	65
9	Conclusions	68
	Literature	70
	Summaries of Papers	89

1 Introduction

Production of nanofibres is a fascinating area and is the focus for a good deal of research activity worldwide. The term nanofibre has many definitions. The *nano* prefix is usually applied to materials having dimension(s) less than 100 nm, but in the case of fibres, the limit can be 0.5 μm or even 1 μm [1-2]. For simplicity, all sub-micron fibres are referred to as nanofibers in the present thesis. The preparation of polymeric nanofibres by means of a method called electrospinning was first patented in 1902 [3-4], and has gained increasing attention in recent decades [5-18]. Competing techniques for the production of polymeric nanofibres are, for example, the use of melt blowing technology, melt-spin production of islands-in-the-sea structured bi-component fibres with a dissolvable polymer as a matrix, and via fibrillation of linear cellular structured fibres such as cellulose into nano-sized sub-fibres or fibrils [1-2, 19], as well as drawing with micropipette, template synthesis, phase separation and self assembly [11]. Despite its limitations, such as relatively low productivity, the electrospinning method remains a promising and intriguing method that enables preparation of nanofibres as a commercial process.

The commercial production of the electrospun nanofibres first started in the former Soviet Union. Petryanov discovered the use of an electric field in the production of filter materials in 1930s and the local filter industry has utilized the technology for the commercial production of the electrospun FP (*Filter of Petryanov*) materials since then without the knowledge of the Western world until recently [20-21]. One of the main applications of the FP materials has been the protection against nuclear-active aerosols, an application which has been particularly important after the Second World War and also after the Chernobyl accident in 1986 [20]. As early as the 1960s, FP materials have been produced in several facilities in the Soviet Union yielding an annual production of around twenty million square metres or six hundred tons. The largest facility at the time was a plant in Sillamäe, Estonia, which still produces electrospun fibre materials commercially and collaborates closely with the Finnish Ahlstrom Corporation [21-22].

Certain western companies have also studied and utilized the electrospinning technique already for several decades with little global visibility. Large nonwoven material and filter manufacturers such as Freudenberg Nonwovens in Europe [23] and Donaldson Company in U.S. [24-29] had already gained their first patents for the production of electrospun media more than twenty years ago. The Donaldson Company¹ utilises the method in its business, and currently produces over ten thousand square metres of electrospun materials per day [30-31]. The era of secrecy is now a thing of the past, and Donaldson also openly publishes information about its research activities and properties of their electrospun filter products [30-34]. Interest in electrospinning has increased in the last ten years and today there are production sites across the world. Companies producing electrospun nanofibres include, for example, Finetex Technology² (Korea), Espin Technologies Inc.³ (U.S.), Nanotechnics Co. Ltd.⁴ (Korea), and Nanofiber Future Technologies Corp.⁵

¹ <http://www.donaldson.com>

² <http://www.finetextech.com>

³ <http://www.espintechnologies.com>

⁴ <http://www.nano21c.com>

⁵ <http://www.nftc.cc>

(Canada). Research into the production and applications of electrospun materials is being carried out at hundreds of universities and research institutes worldwide.

Most nanofibre producers as well as research institutes have constructed their own electrospinning equipment, but today there also exist manufacturers of small and also larger-scale electrospinning equipment. The Nanospider technology, which has been developed jointly by the Technical University of Liberec and Elmarco Company⁶ (Czech Republic), was applied to the industrial production of nanofibres in 2006 [35-36]. Other equipment manufacturers include NanoStatics⁷ (U.S.), Kato Tech Co. Ltd.⁸ and Fulence Co. Ltd.⁹ (Japan).

In electrospinning a polymer containing liquid, typically a solution, is drawn into fibres utilizing electrostatic forces. Simple electrospinning equipment for laboratory use consists of a nozzle, a collector and a voltage source [37]. The nozzle can be a syringe, a needle [37] or some other kind of capillary, but also nozzleless designs are possible [35]. The collector is typically a plate, but it can also be, for example, some kind of dynamic collection device [37]. Typically voltage, which is applied between the nozzle and the collector, has a magnitude of some tens of kilovolts. The solution is drawn from the nozzle towards the collector by means of an electric field, and it first forms a shape known as Taylor cone [38]. When the electrical forces exceed a critical limit, a solution is ejected from the tip of the cone and the jet is accelerated towards the collector. The polymer jet undergoes instabilities such as whipping [39-44], and thus the nature of the jet's path is often described as chaotic, and fibres form a randomly oriented fibrous web on the stationary collector plate. The fibre formation is based on interactions between polymer chains. The high polymer concentration or the high molecular weight of the polymer ensures a sufficient amount of chain entanglements to keep the jet of the polymer solution coherent during the vigorous, unstable electrospinning process. The fibre diameters are typically in the sub-micron range, which is smaller than that achieved using conventional fibre drawing methods [6, 15]. This is possible because the mutual charge repulsion caused by the electric force overcomes the surface tension [45], which would restrict the surface area of fibre and, thus, limit the drawing ratio in the conventional fibre forming methods.

The specific surface area of the electrospun fibres is high, typically approximately 300 m²/g, due to the small fibre diameter, and the length of the electrospun fibres can easily be many kilometres [15]. Characteristically, electrospinning forms a randomly oriented fibre mesh, but different kinds of fibre assemblies can also be achieved by modifying the electrospinning design [37]. In addition to typical random fibre mesh, these assemblies include, for example, aligned fibre mesh, patterned fibre mesh, random 3D structures, and sub-micron spring and convoluted fibres [37]. Tsai *et al.* [46] have listed some potentially attractive properties and also problems associated with the electrospinning method. The list of the attractive features includes very soft hand, barrier properties against micro-organisms and particulates, good strength per unit weight, high surface energy, processing at room temperature with simple equipment and low energy consumption.

⁶ <http://www.elmarco.com>

⁷ <http://www.nanostatics.com>

⁸ <http://www.keskato.co.jp>

⁹ <http://www.fulence.co.jp>

Potential problems, on the other hand, are insufficient wetting and wicking, weak web strength, impossibility of coloration of fibres and low production rate [46]. At 0.3 g/nozzle or hole/hour [2], the nanofibre production rate of electrospinning is only around one percent of those of competing fibre production methods, melt-blowing and multi-component spinning/separation at 0.5 g/nozzle or hole/minute [2].

One interesting feature of electrospun nanofibres is that the properties of the material can change dramatically when its dimensions are reduced to the nanometre scale [47]. These small dimensions might provide unexpected properties different from those of the bulk material. Naraghi *et al.* [48] observed that even though the ultimate strength of the electrospun nanofibres was comparable with one of the larger fibres, the tensile strength and the behaviour in strain was unusual. Fennessy *et al.* [49] suggested that electrospun nanofibres outperform their conventional counterparts as a reinforcement component because of their increased surface area and high length-to-diameter ratio. Electrospun fibres can be prepared from a wide variety of polymers, but materials of electrospun fibres are, however, not limited to neat or blended polymers. Electrospinning can be conducted in the presence of additives. The use of additives can be roughly divided into two groups according to purpose. First, they are used to influence the electrospinning process, and second, to modify the properties of the electrospun fibres. Sometimes, however, the boundary between the two groups is unclear since many additives affect the process and the properties of fibres alike. Electrospun fibres can be functionalized using additives, and fillers of many kinds can be used to form composite fibres [13, 50]. Metal-containing nanofibres, for example, can be pyrolysed to ceramic nanofibres, and organic nanofibres graphitized to carbon nanofibres [15]. Typically, electrospun nanofibre webs have high porosity [51] with a tortuous pore structure and good interconnectivity of the pores [52], which can be utilized in many applications.

Due to the countless possibilities of materials and the many potential structures, electrospun nanofibres can be utilized in a wide variety of technical applications fields [8, 13-14, 18]. Biotechnology and environmental engineering utilizes electrospun materials in filters and membranes [22, 24-28, 30, 32-34, 51-104]. Electrospun nanofibres can be used as reinforcement in composite materials similar to microfibres [8, 49, 104-107]. Electrospun fibres can also be used in defence and security applications such as chemical and biological protection [34, 59, 74, 100, 108] as well as sensor applications for security or other purposes [109-116]. In the healthcare sector electrospun fibres have many potential applications. They can be used, for example, in tissue engineering [117-134] and wound dressings [134-135]. Electrospun fibres containing photoactive fullerene derivatives have potential applications in photodynamic cancer therapy and in the treatment of multi-drug resistant pathogens [136]. Drug delivery materials can be prepared by including medicines into an electrospun structure [124-125, 137-142], and even living cells can survive the electrospinning process [143]. Modified electrospun fibres can also be used in energy storage applications, including photovoltaics such as solar cells [144-147], fuel cells [148-151], and batteries [149], and catalyte-containing electrospun nanofibres are suitable for a variety of catalyst applications [55, 99-100, 149-158]. Electrospun fibres of intrinsically conducting polymers [147, 159-168] as well as conducting composite fibres [169-172], photoluminescence fibres [172-173] and light emitting fibres [174] may be utilized in nanoelectronics and optoelectronics. The flexibility of conducting electrospun fibres enables their use in

wearable electronics [175]. The sound absorption [176] and heat transfer properties [177] of electrospun fibre mats provide scope for their use in sound and thermal insulation. Electrospun fibres from removable polymer can be used as fibre templates in the preparation of nanotubes with TUFT (*Tubes by fibre template*) process [178-182]. The surface morphology of the electrospun coating might enhance hydrophobicity, and electrospun coatings can be used to form super hydrophobic surfaces [183-184] that can also have self-cleaning properties [183]. Applications of electrospun fibres as surface treatment can also be found in the paper industry [29, 185-186].

In filtration electrospun nanofibres can significantly enhance product properties. Performance of a fibrous filter is mainly dependent on the size of the particles, the velocity of the air flow, the size of the fibres and the packing density of the filter media [187]. Improved filtration performance can be seen especially in HEPA (*High efficiency particulate air*) and ULPA (*Ultra low penetration air*) filtration¹⁰, since the ability of the electrospun fibres to capture sub-micron particles is better than that of the larger fibres used in conventional filters [18, 87]. Conventionally HEPA and ULPA filters are made of glass fibre paper, consisting of fibres with sub-micron range diameters [188-189]. Glass fibres have certain disadvantages such as fragility in processing, weight, large pressure drop, and skin irritation. They can not be charged and, thus, the electric separation method cannot be employed. Other viable nanoporous materials for HEPA and ULPA filters are ceramic membranes [190], expanded polytetrafluoro ethylene (PTFE) [191], and, of course, polymeric nanofibres [22, 53]. The use of the polymeric nanofibres instead of glass fibres permits a lower weight of filter media, potential savings in materials costs, smaller pressure drop, and thus also smaller energy consumption [188]. The nano-scale fibre diameter and also the high specific area of the electrospun materials are well-suited for filtration applications. The dramatic increase in filtration efficiency due to a thin layer of electrospun fibres on conventional filter media can be seen with a relatively small or almost immeasurable decrease in permeability [33].

1.1 Objectives and Approach

The aim of this study was to understand the electrospinning method at a scientific level in order to apply the method to the continuous manufacturing of air filtration materials, especially with regard to selected polymers including polyamides. The targets of the studies were, firstly, to produce nanostructured fibre composites and, secondly, to produce materials of such a composite suitable for air filtration. In this thesis the electrospinning method is utilized in the preparation of nanofibre composites with various compositions. Many properties of electrospun fibres are examined for their suitability for use in filtration applications. The preparation of a nanostructured fibre composite can be conducted with small laboratory scale electrospinning equipment capable of forming fibres. However, production of the material for the filtration application requires the scaling-up of the electrospinning. Scaled-up equipment needs to be capable of forming larger fibrous webs in a controlled manner. Thus, in addition to the formation of fibrous

¹⁰ According to EN 1822 "*High Efficiency Air Filters (HEPA and ULPA)*" the ranges of the collection efficiencies for the particle size with the highest penetration of the HEPA and ULPA filters are 85 % - 99.995 % (classes H10-H14) and 99.9995 % - 99.999995 % (classes U15-U17), respectively.

nanostructured materials and their use in filtration applications, the scope of this thesis also deals with issues relating to the scaling-up of the electrospinning process,

The electrospinning method is related to the electrospray method, but the focus of this thesis is on the actual spinning, or in other words the formation of fibres, except for occasional comparative observations. The electrospinning technique is applicable to polymer solutions and melts, but in the present thesis the interest is exclusively solution electrospinning, unless otherwise stated. Electrospinning is typically conducted using nozzles, capillaries or orifices through which the solution is fed, and from which the jetting occurs. The jetting and fibre formation can also occur from a free liquid surface without the nozzles. The nozzleless designs are briefly reviewed here, but the basic approach is centred on electrospinning with the nozzles, the method used in all reported experiments. The approach of this thesis to electrospinning includes scaling-up of the process and, thus, also commercial production. Commercial production issues, such as achieving improvements in productivity and an uninterrupted manufacturing process are also considered, despite the fact that the trials were mainly conducted on a laboratory scale. The ultimate purpose of this thesis is to obtain materials suitable for air filtration, though some of the nanostructured fibre composites studied in the papers of this thesis are also intended for the other application fields. Since the main focus of this thesis is air filtration, the filtration of liquids with electrospun materials is discussed only briefly.

1.2 *Structure of the Thesis*

This thesis is based on six scientific papers published in refereed journals. It also contains an extended summary which consists of a literature review and an experimental section. The literature review establishes the current state of research in the field of electrospinning within the scope of this thesis. It is divided into three parts: Chapter 2 presents the electrospinning method, Chapter 3 presents the nanofibre composites formed by the electrospinning method, and Chapter 4 presents the methods for the preparation of the fibrous web, and the use of such webs in filtration applications. The literature review was conducted using available material from the early trials relating to electrified liquids up to 2007. Later sources, published in 2008, were excluded from the review.

The experimental part consists of several separate studies reported in six papers, which are included as annexes to this summary as Papers I - VI. Chapter 5 summarizes the main experimental methods used in these studies and also includes more detailed descriptions of two customized methods. The main results from the papers concerning the topic of this thesis are presented and discussed in three parts: Chapter 6 presents the formation of the electrospun fibres from neat polymers and composites, Chapter 7 the formation of the nanofibre layer, and Chapter 8 the use of the nanofibre composite in the filtration applications. The conclusions are discussed in Chapter 9.

2 Electrospinning Method

The first patents for the technique, formerly referred also to as electrostatic spinning and currently known as electrospinning, were published in 1902 [3-4]. During subsequent decades interest in this method was mainly expressed in terms of issued patents, since the real applications were rare until the current millennium. There was, however, some research activity during the last century. Formhals [192-201] was one of the early pioneers in the Western world in the 1930s. He is often credited with the invention of the method despite the earlier patents of Cooley [3], Morton [4] and Hagiwara [202]. Research into the electrical phenomena of liquids in an electric field started earlier. For example in 1880s Lord Rayleigh [203] published his studies on the equilibrium of charged liquids. Similar research continued in the last century, notably by Zeleny [204], who published his studies on electrical discharge from liquid surfaces in the 1910s, and Taylor [38], who studied electrically induced jetting from the surface of a viscous liquid in the 1960s. In the 1970s Baumgarten [205] published his studies into electrospinning of polyacrylo nitrile (PAN), and Simm *et al.* [89-90] filed patents describing electrospinning equipment. In the 1980s Larrondo and Manley [206-208] published their research on melt-electrospinning of polyethylene (PE) and polypropylene (PP). Development of fine fibre production was also being conducted in secret in the Soviet Union by Petryanov, who discovered the technique in 1936 and whose name is still used for electrospun filter materials known as FP - filters of Petryanov [20]. Petryanov and his research team were awarded the Lenin Prize for their work with FP in 1966 [20]. More recently such research continues at the Aerosol Department of Karpov Institute of Physical Chemistry where it is now published openly [77, 92-95, 209].

In the 1990s nanotechnology began its global rise in several fields of technology, and research into electrospinning increased after Doshi and Reneker [5] published their work in 1995. Since then Professor Reneker of the University of Akron (U.S.) has been one of the most prolific contributors to the literature on electrospinning. His publications deal with topics such as clarifying the instabilities and other phenomena occurring during the electrospinning process [39-40, 210-213], presenting the different morphologies obtained in electrospinning [6, 214-221] and modelling of the fibre formation [222-223]. Major research has also been carried out in Natick, U.S. Army Soldier Center [59-63, 108, 168, 224]. In recent years there has been a rapid growth in the number of publications dealing with the electrospinning process and electrospun fibres, as can be seen in Figure 1. One important group of publications provides a profound understanding and modelling of the process and its phenomena, an area which, in addition to Reneker, has also been studied by others such as Hohman *et al.* [41-42] and Shin *et al.* [43-44]. Another major theme of the publications is parameter studies. Here the effects of different variables on electrospun fibres and on the electrospinning process are determined in general or for specific polymers. Deitzel *et al.* [225] and Theron *et al.* [226-227] have, among others, published studies dealing with the influence of electrospinning parameters on the formation of fibres and the electrospinning process. At the same time there is also considerable research interest in the potential applications of the electrospun fibres. Huang *et al.* [8], Ko [9], Li and Xia [10], Subbiah *et al.* [12] and Ramakrishna *et al.* [14] have published extensive surveys of the advances in electrospinning method and its potential applications. Teo and Ramakrishna [37], for their part, have evaluated various electrospinning designs and nanofibre assemblies.

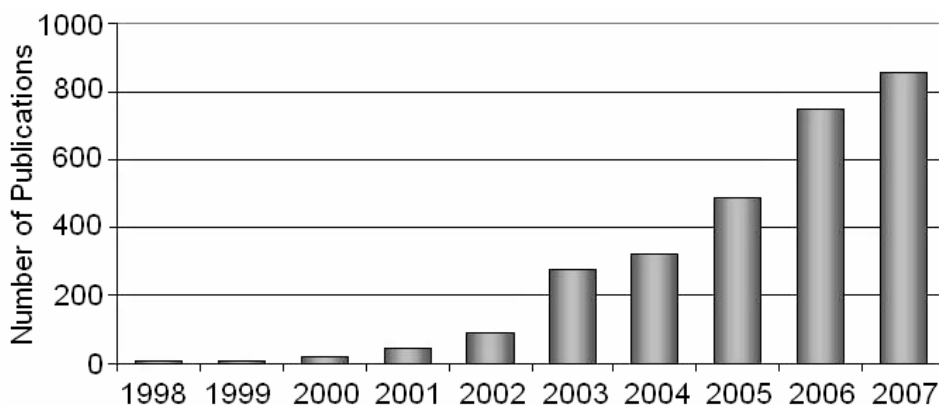


Figure 1. Increase in the number of publications on electrospinning over a ten year period. (Source: SciFinder Scholar, 11.4.2008, search using keyword 'electrospinning' gave 3138 answers, which were assorted by publication year).

The electrospinning method is closely related to electrospraying, which is also termed electrohydrodynamic (EHD) spray [228-237]. In both methods a polymer solution is fed through a nozzle and attracted towards the collector electrode using electrostatic forces until jetting occurs from the surface of the droplet. The jet undergoes instabilities, which together with the solution properties determine the morphology of the forming nano-sized structures obtained onto the collector. A schematic illustration of the process is presented in Figure 2a. When the jet breaks up into droplets, the process is called electrospray, and if the viscoelastic forces can hold the jet coherent and fibrous structures are formed, the resultant process is known as electrospinning. Just above the fibre forming limit there is an operating window producing both morphologies, droplets and fibres, and their combination, beaded fibres, see Figure 2b. Beaded fibres are formed when the fibre structure is not completely stabilized during electrospinning and the jet resists the extensional flow [238]. An increase in stabilizing viscoelastic forces, caused by increased concentration, reduces of the amount of the beads and enlarges the fibre diameters. Simultaneously, the beads merge into the growing fibres, and finally smooth fibres with round cross-sections are obtained. This kind of *change in morphology* is typical of electrospinning [159, 214].

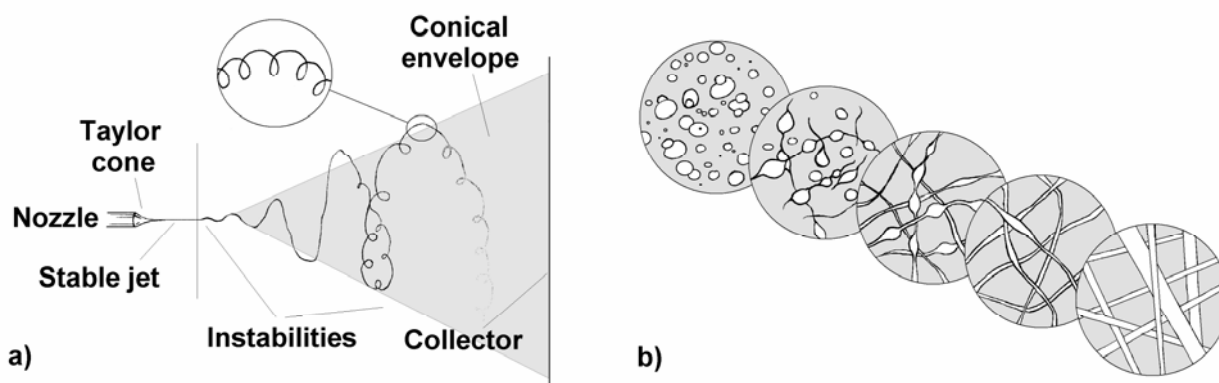


Figure 2. a) A schematic illustration of the electrospinning process. Jetting occurs from the Taylor cone. After a short stable stage, instabilities start to bend the jet, which eventually leads to 3D looping within the envelope cone. Secondary and tertiary looping can also occur before the jet reaches the collector. b) Typical change in morphology from droplets through beaded fibres into smooth fibres occurring with increasing concentration.

Further rises in the viscoelastic forces increases the fibre diameters and may eventually lead to the occurrence of flat, ribbon-like fibres [159, 238]. The ribbon-like fibres are obtained when the surface of the fibre solidifies faster than the inside, and the skin-like structure collapses when the solvent is completely removed from the inner parts [215, 220, 239]. In the upper limit of the fibre forming range, the solution is prone to dry on the nozzle [5, 240-241] and the high viscosity prevents the continuous flow of the solution through the nozzle [242], thus suppressing the electrospinning process.

This chapter considers the electrospinning method starting from the properties of the polymer solution in Chapter 2.1, proceeding to the formation and the instabilities of the jet in Chapter 2.2, and finally to the properties of the forming fibres in Chapter 2.3. In addition to the fibre formation process, the various electrospinning designs are presented in Chapter 2.4, and the modelling of the electrospinning process in Chapter 2.5.

2.1 Polymer Solution

The properties of the polymer solution have a major influence on the electrospinning process. The present section discusses the importance of certain major solution properties such as viscosity of the solution, the amount of chain entanglements and the conformation of the polymer chains in solution, as well as solvent properties.

Viscosity, which measures the resistance of the fluid to flow, plays an important role in electrospinning, since it stabilizes the jet. Viscosity is directly proportional to the concentration of the solution and to the molecular weight of the polymer. This relationship has an accelerating pitch, which can, for example, follow an exponential growth [243] or a power law equation [139, 244]. The concentration, the molecular weight and the viscosity form a trinity of parameters, all affecting the fibre forming ability of the solution, also termed *electrospinnability*. According to McKee *et al.* [245] and Shenoy *et al.* [246] the chain entanglements can be used instead of these three parameters when evaluating fibre formation, since a certain amount of the chain entanglement is needed to keep the solution jet coherent during the electrospinning [246]. In solution the flexible polymer chain takes a random coil conformation [247], each of the chains occupying the space of a sphere having a dimension of R_g (*radius of gyration*) [247]. In the dilute concentration regime the polymer chains are distributed randomly as separate spheres with only a few interchain entanglements [217], see Figure 3a. These separated chains behave more or less independently, and the polymer molecules primarily interact with the solvent molecules [247]. When the whole volume of the solution is occupied by these spheres, the overlap concentration (C^*) is achieved [247]. Above C^* the polymer chains are overlapping, entanglements are increasing, and chain mobility is greatly reduced, see Figure 3b. This regime is called semidilute, and its existence is characteristic of polymer solutions [247]. The chain coils are still distinguishable, but touch and interact with each other to cause a higher amount of entanglements and much higher viscosity compared to dilute solutions [217, 247]. The intersections between different chains are called entanglement points. Entanglement concentration (C_e) is located within semidilute regime, dividing it into unentangled and entangled sub-regimes [248], for example with polymethyl metacrylate (PMMA) this crossover has found to occur at $C/C^* \sim 3$ [249]. Below C_e the solution viscosity is controlled by the

intramolecular excluded-volume effects, while above C_e the intermolecular entanglements have a dominant effect on the rheology of the solution [248] enabling the formation of beaded fibres [245]. The formation of bead-free fibres occurs in concentrations $2-2.5 \times C_e$ [245]. Shenoy *et al.* [246], for example, obtained stable fibre formation of bead-free fibres when there were 2.5 entanglements per chain. The broad molecular weight distribution can increase the concentration needed to obtain the uniform, bead-free fibres [249]. The larger the molecular weight of the polymer is, the broader is the range between the C^* and C^{**} , which is the upper limit of the semidilute regime. Above C^{**} monomers are congested and the solution is in concentrated regime [247].

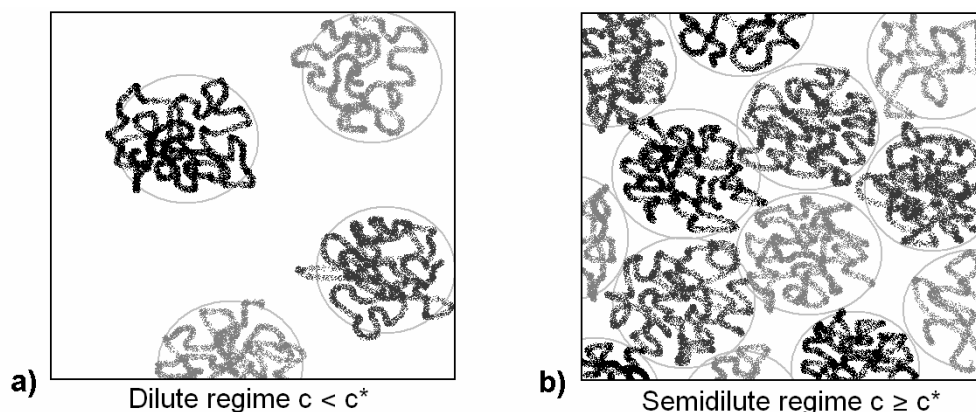


Figure 3. Dilute (a) and semidilute (b) concentration regimes.

The structure of the polymer and the conformation of the polymer chain in solution affect the amount of the chain entanglements. Branching of the polymer, for example, increases C_e/C^* compared to the linear polymer of equivalent molecular weight [245]. The branched polymer may have higher molecular weight, but still lower viscosity than the linear polymer of the same species [250]. Hyper branched polymers may not be able to form nanofibres at all due to the lack of chain entanglement [250]. The concentration regimes of rigid chain polymers are different compared to a linear flexible chain; the C^* is much lower. Electrospinning of polyelectrolytes, such as chitosan, containing charged atoms in their chain structure can also be more challenging than electrospinning of neutral polymers [251-253]. The chain conformation of polyelectrolyte in solution depends on the presence of counter ions in solution, and they can, depending on the conditions, take on a contracted rod-like or globular shape instead of the random coil conformation. Therefore the viscoelastic behaviour of the polyelectrolytes, along with the scaling laws of their concentration regimes, differs significantly from those of the neutral polymers [254]. The increased conductivity, caused by charged species within the chain and solution of the polyelectrolyte, affects the spinning process and may also enhance the fibre formation [254-255].

The quality of the used solvent affects the electrospinnability of the polymer solution, since it affects the intermolecular interactions, the conformation and size of polymer chain [247] and, thus, the viscosity of the solution [242]. Lu *et al.* [256], for example, found that the flexibility of the molecule chain, which depends on the solvent, is a crucial factor in electrospinning. Solvents which are able to dissolve a given polymer well are called good solvents, while those that do not dissolve it are called non-solvents. The polymer concentration

in a good solvent can be as high as 100 % and the solution can still remain clear and uniform [247]. Dissolution happens when solvation lowers the free energy of the system, which means that good solvents lower the free energy and non-solvents increase it [247]. The mixing of solvent and polymer changes the overall interaction energy of the system through the rearrangement of contacts. Separate components have only polymer-polymer or solvent-solvent contacts, but after mixing, these contacts are partly replaced by polymer-solvent contacts. Molecules of a good solvent preferentially surround the polymer chain, while in a poorer solvent the polymer-solvent contacts are more unfavourable and the polymer chain is contracting. Probability of contacts is expressed by the χ (chi) parameter, also known as Flory's χ parameter or Flory-Huggins χ parameter [247]. A positive χ indicates that the polymer-solvent contacts are less favoured than the contacts between the molecules of individual components. A negative χ means that polymer-solvent contacts are preferred, which promotes the solvation. Magnitude of χ decreases with increasing temperature thus enhancing the solvation, but it is also influenced by the characteristics of each polymer-solvent system [247]. In a binary polymer-solvent system the interaction between polymer molecules can be, depending on the type of solvent, either attractive or repulsive. If random coil conformation of the chain changes to globular shape, for example due to the poorness of the solvent, the amount of the monomer-monomer contacts within one chain is maximized. This enables gelation, but might prevent fibre formation in electrospinning because the interchain entanglements are lacking.

Nonetheless, the goodness of the solvent is not the only parameter affecting the suitability of the solvent to electrospinning. Pattamaprom *et al.* [257] studied the electrospinnability of polystyrene (PS) with eighteen different solvents. They observed that solvents having a high degree of electrospinnability typically had density less than 1 g/cm³ and viscosity lower than 1.5 cP. Good solvents also contained carbonyl groups (C=O), resulting in a high dipole moment [257]. Eda *et al.* [248] noticed that used solvent, and especially its dielectric constant and evaporation rate, played an important role in determining the physical phenomena of the formation and the instabilities of the jet. The properties required from a solvent listed by Wang *et al.* [258] are good miscibility with polymer, low boiling point, low surface tension and high conductivity. Low boiling point of the solvent may also cause problems since the high evaporation rate may cause blocking of the nozzle [242, 259-260] and reduce the mobility of polymer chains in solution jet, which may lead to bead formation [261]. The viscosity of the solution is typically directly proportional to the polymer concentration [243, 262], while the other solution properties may be dominated by the properties of the solvent. Wang *et al.* [258], for example, noticed that the surface tension of the solution remained intact regardless of the polymer content. Conductivity of polymer solution, which is considered to be ionic in nature [39], is determined by solvent and polymer molecules as well as possible additives, which can act as charge carriers in solution.

Even though electrospinnability is typically explained in terms of the chain entanglements, this approach is, however, inadequate to explain fibre formation in all systems. For example, in systems with polymer capable of physical gelation, the stabilization of the jet may be achieved by the combination of the thermo-reversible junctions and the chain entanglements [263]. In such systems ionic and hydrogen bonds might be so strong that the electrospinnability threshold is lower than that predicted on the basis of chain entanglements alone [263]. The effect of hydrogen bonds between polymer chains on the fibre morphology was observed by

McKee *et al.* [264]. The unexpectedly large fibre diameters were the result of the strong hydrogen bonding, since they increased the apparent molecular weight of the polymer [264]. Yu *et al.* [265], on the other hand, demonstrated that the elasticity of the solution is more closely associated with fibre morphology than the Newtonian shear viscosity of the solution. They also stated that merely strong elasticity can keep the jet coherent, and the presence of the entanglements is not required for the formation of uniform fibres. If relaxation time (τ) of the fluid is longer than the time of the extensional deformation, the elastic response needed to suppress the Rayleigh instability (see Chapter 2.2) and to keep the jet coherent, is achieved [265]. Drew *et al.* [266] emphasized the importance of viscosity in fibre formation, but they have shown that fibres can be formed in cases when the requisite viscosity is achieved with insoluble filler such as nano-sized titania (TiO_2) particles and not with chain entanglements. The requirements determining the electrospinnability of certain solutions seem to be in dispute.

2.2 Formation and Instabilities of the Jet

The electrospinning method utilizes an electrostatic field. Electrical forces enable jetting and the development of instabilities. These electrically induced phenomena are discussed below.

Charging of the polymer solution is the essence of the electrospinning process since it enables jetting, carries the jet in the electric field and causes the instabilities which promote the stretching of the jet. Charging enables the viscous solution to pass through a capillary tube, which ordinarily would be too narrow for the solution [4]. Charging also accelerates evaporation of solvent, promoting drying and solidification of fibre [4, 161]. Charging can be conducted, for example, by immersing a high voltage electrode inside the nozzle or attaching it to the metallic capillary. Hohman *et al.* [42] suggest that the charge transport mechanism near the nozzle might be advection of the charge density built up around the nozzle. Rutledge *et al.* [267], on the other hand, suggest that the charging of a polymer solution might be a combination of induction and frictional charging.

When a polymer solution is fed into a nozzle and there are no external forces affecting it, it typically forms a hemispherical pendant droplet or meniscus at the orifice of the nozzle. The shape of the charged droplet depends on the balance between the surface tension, the hydrostatic pressure, and the electric forces [268]. Charging of the pendant droplet attracts it towards the collector and causes it to gain a stable conical shape, usually referred to as the Taylor cone [38, 211]. In practice the shape is rather quasi-conical with a spherical tip [269] or hyperboloidal [211]. The sharpness, or the half angle, of the shape depends on the elastic forces and surface tension of the solution [211]. Jetting occurs when electric forces at the tip of the droplet are no longer balanced by the surface tension [45, 268]. Solutions of low molecular weight species are more prone to atomization, which reduces the half angle of the cone and perturbations. This may lead to premature jetting and failure to obtain stabilization of the shape [211].

Jetting of the polymer solution from the droplet can occur in different modes. Jetting in electrospraying has been widely studied [228-237], and classification of electrospray modes have been discussed by Cloupeau and Prunet-Foch [230-231], Shiryayeva and Grigorev [234], as well as Javorek and Krupa [236]. The

operating range for each electrospray mode can be determined in terms of voltage and flow rate [236], but it might also be affected by other factors such as conductivity of the solution [237]. The size and charge of forming droplets depends on the mode [236]. In some modes spray forms directly from the pendant drop, but the mode classification by Javorek and Krupa [236] also includes five modes (out of ten) involving the formation of jet(s) prior to its subsequent disintegration into droplets. Cone-jet mode is the most stable of the modes. In this mode the initial jet is straight and linear, while other modes involve oscillation or rotation of the jet, or the occurrence of multiple jets [236]. Even though the amount of modes in electrospinning is smaller [225], different modes can still be found. Samatham and Kim [270] distinguished four electrospinning modes for jet formation and the electrical current. These modes are fluctuating jet, stable jet, stable jet with polymer drops and multiple jets regime. In stable jet mode the solution flow corresponds to the fibre formation speed, and the shape of the pendant droplet remains constant. Discontinuous jet can be caused by too low a solution flow because there is insufficient solution in the tip of the nozzle, or too high a solution flow when excess solution is dripping from the nozzle. Too high a solution flow can also lead to formation of multiple jets. Change of mode can be achieved by changing the voltage, which affects the speed of the fibre formation. Jetting mode affects the quality of the fibre in terms of diameter distribution and occurrence of beads [270].

The size of the nozzle and the size of the droplet are on a millimetre scale [42], but the initially formed single jet typically has a diameter of some hundreds of micrometres [40, 222]. As the polymer jet travels through the external electric field its diameter decays asymptotically, leading to nanometre scale diameters [271]. The solvent evaporates from the jet and the evaporation is enhanced by the electrical charge [4, 161], but there is a huge decrease in diameter during the electrospinning process which is not attributable only to the removal of solvent. Stretching of the jet is caused by the electrical forces; the effects of gravity and aerodynamics are negligible in electrospinning [39]. During the electrospinning process the jet can split or splay into multiple thinner filaments [5, 39]. Splitting has been observed with high speed camera images of the jet [39, 212] and also images of electrospun fibres [215, 272]. The occurrence of splitting, however, is too rare to explain the small fibre diameters [39]; it is widely accepted that instabilities are largely responsible for the high stretching of the jet and the huge decrease in the diameter [44]. In the initial stage the jet is straight until, at the critical point, the perturbations destroy the straight movement and the instabilities emerge [273] as presented in Figure 2a on page 7. The unstable, stretching jet has been studied by modelling [39, 41-43, 274] as well as on-line observation, for example, with high speed and video cameras [39, 212, 248, 275-277] or using interference colour techniques [213].

Two opposing forces affect the jet: 1) the surface tension, which stabilizes the jet and tends to minimize its surface; and 2) the charge repulsion, which destabilizes the jet and increases its surface [261]. And during electrospinning, three distinguishable competing instability modes can occur: 1) a classical (axisymmetric) Rayleigh break-up instability mode, 2) an axisymmetric conducting instability mode; and 3) a whipping conducting instability mode [41-42], also known as bending instability [39-40]. The dominant mode is largely determined by the surface charge density, the radius of the jet, the flow rate of the solution, and the properties of the fluid such as viscosity, dielectricity and conductivity [41-43]. Many solution and process

variables affect these properties and, therefore, may also affect the mode. Conducting modes, especially whipping, are enhanced with increased voltage and electric field strength, while Rayleigh instability is suppressed by them [41, 278].

Both the classical Rayleigh break-up instability and the conducting axisymmetric instability are axisymmetric, or in other words, varicose in nature and, thus, responsible for modulating the radius of the jet as well as the bead-like structures of the forming fibres [18, 42, 278], see Figure 4a. The Rayleigh instability is driven by the surface tension [265, 278]. It is favoured by the high surface tension [278] and it can be stabilized by the viscoelasticity of the solution [265]. Axisymmetric conducting instability mode involves electrical competition between the free charges and the electric field, and it is independent of the surface tension [41]. The modulating radius of the jet modulates the surface charge (σ) of the jet. The modulating surface charge causes tangential stress and leads to the instability [41]. The high surface charge density suppresses the varicose instability and favours the whipping mode, and the surface charge density increases with increasing conductivity [41-42].

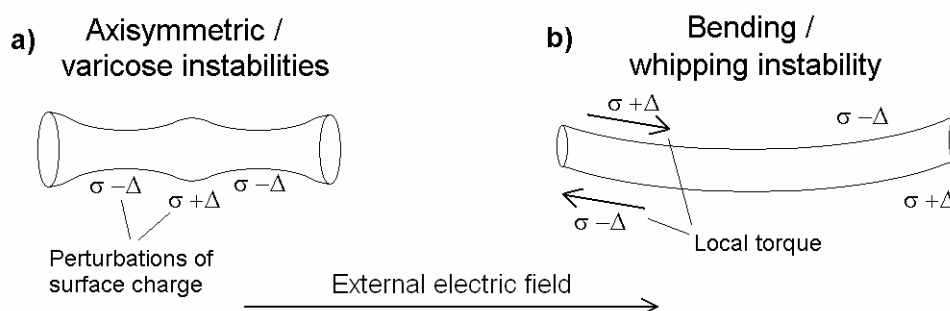


Figure 4. Axisymmetric (a) and bending instabilities (b) of the jet in external electric field. [44]

The whipping instability is very characteristic of electrospinning and makes the jet oscillate from the centreline of the jet [41-42]. At the beginning the jet is stable, however, after a short while it starts to bend back and forth prior to actual looping in three dimensions, see Figure 2a on page 7. The circumference of the loop increases in each cycle, forming the envelope cone. Secondary [39] and tertiary looping of the jet [222] have also been observed. There are two mechanisms inducing the whipping instability. Firstly, the whipping occurs when charges of the jet form a dipolarized charge distribution and these dipoles interact with the external electric field causing torque [43]; see Figure 4b. Secondly, the mutual repulsion of the surface charges also causes the bending of the jet [43]. The onset point of the whipping depends on factors such as the elasticity of the solution. Whipping is fiercer with lower elasticity and shorter relaxation times (τ), and smaller fibres can be achieved [256]. Yu *et al.* [265], for their part, have determined the dependency between the onset of the whipping and the radius of the jet. Whipping started when the radius of the jet was reduced to the range of 10 μm - 20 μm [265]. Whipping is enhanced by the high surface charge density [42] and stabilized by the surface tension and the viscoelastic forces [39, 265]. Due to the whipping instability, the path of the jet is complicated and much longer than the distance between the nozzle and the collector. The long path of the jet can also be seen in the collection speed of nanofibres, which can be six orders of magnitude higher than the flow speed of the solution in the nozzle [279], being as high as 3.5 km/s [222].

Due to the instabilities the path of the jet and the envelope cone (see Figure 2a on page 7) widen towards the collector, and fibres from a single-nozzle can be deposited onto a relatively large area on the stationary collector.

The conductivity of the fluid and the geometry of the electric field both affect whipping, since its character depends on whether the local electric field near the jet is dominated by its own charge or the tangential electric field [41]. The conductivity of the solution increases the charge density of the jet and thus enhances whipping and the elongation level of jet [42, 280]. The conductivity of a polymer solution is considered to be ionic in nature [39] and it affects the whipping through the charge density, but electric current due to this ionic conduction is assumed to be small and negligible in the electrospinning process [271, 281]. In electrospinning the current, which is typically a few microamperes [222], depends on the flow rate [42, 282]. The roughly linear relationship found between the two [42, 271] indicates that measured current is mainly caused by the mass flow of the charged jet, not the actual electrical conduction, but the nonlinear relationship [282] indicates that other factors also affect it. The current of electrospinning has also been found to be directly proportional to the voltage and to the conductivity of the solution [42]. Current can be used as control variable in electrospinning since different jetting modes can be distinguished from on-line current measurements of the electrospinning process [270].

A certain amount of charge carriers is needed in the solution to enable electrospinning. Hayati *et al.* [228-229] studied discharge and jetting from the electrospray nozzle, and noticed that a stable jet with a conical pendant droplet was only obtained with semi-conducting liquids. Charging did not disrupt the surface of the insulating solution due to the lack of free ions and [229], while highly conducting solution, on the other hand, produced very unstable spray [229]. Reneker *et al.* [39] also observed that with lower conductivity, longer time might be required to reach the surface charge density needed for jetting. Shin *et al.* [44] concluded that the amount of charge transferred to the jet depends not only on the properties of the solution, but also on the equipment and, more specifically, the geometry of the high voltage electrode. In addition the used polarity has an effect on the process and fibre morphology. The optimum polarity leading to smaller fibres depends on the polymer-solvent system [262, 283] and the quality of charge carriers present in the solution. It has been suggested that electrons may disperse into solution more uniformly and more rapidly compared to positive ions because of their smaller size [283]. However, positive voltage seems to be more suitable for most polymer solutions.

The formation of the static electric field is typically obtained using a DC (direct current) power source, which is usually connected to the nozzle or solution. The collector is either grounded or oppositely charged. In laboratory scale equipment the nozzle is typically pointed and the collector is a plate. The electric field in this kind of point-plate design is inhomogeneous, see the field line presentation in Figure 5a. In the plate-plate geometry, where the nozzle is replaced with just an orifice in the middle of another plate, the field is more homogeneous [41], see Figure 5b. The charged whipping jet generally follows the direction of the field lines, but the whole system is dynamic and dependent on its development history. The moving jet has kinetic energy and the mass units of the jet are chain dependent on the previous and next mass units, as well the

charge interactions between the mass units. An auxiliary cylindrical electrode around the nozzle [127, 284-285] or around the jet [286] can be used to stabilize the jet. In consequence, the fibre diameter has been found to increase [284] and fibre deposition area to narrow [286], see Figure 5c. During electrospinning a space charge may be accumulated around the pointed nozzle due to electrical discharges from it. If corona streamer discharge occurs, it ionizes the air around the point. When the point is charged positively, highly movable electrons are quickly returned to the point and a cloud of positive ions remain around the nozzle forming a space charge [287]. This may hinder the jetting from the pointed nozzle.

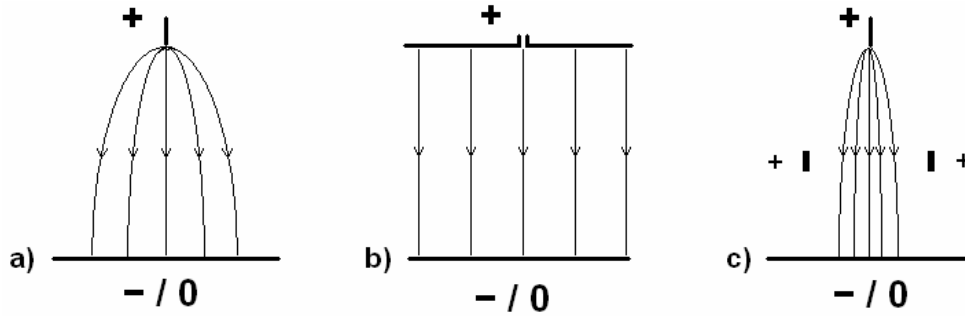


Figure 5. Fields of electrospinning: a) point-plate design, b) plate-plate design and c) effect of auxiliary electrodes.

The deposition of the electrospun fibres onto the stationary collector is typically random due to the chaotic motion of the jet [286]. The shape and size of the deposition pattern depend on the electrospinning parameters. Mode of electrospray has been found to affect the distribution of aerosol and thus the deposition pattern [236], but in electrospinning the viscoelastic forces of the solution also affect the deposition. The general shape of the deposition pattern in the case of single-nozzle and square collector is round [106, 159], but in addition to the round, even pattern, the fibre quantity can form various circular configurations [Paper IV, 288] (see Figure 6). The uneven deposition of fibres has been observed by Barhate *et al.* [52], though they provide no explanation for this phenomenon.



Figure 6. Typical shapes of the deposition patterns: a) round, b) ring, and c) bulls eye.

Our model [Paper IV], on the other hand, clarifies this and is presented in Chapter 7.1. The levels of the directional field components of the electric field vary in the different parts of the field causing the phenomenon. Size of deposition area depends, for example, on voltage, distance and solution viscosity [58, 106]. Voltage induces the whipping and affects the widening angle of the envelope cone and, therefore, the distance also affects the area. The envelope cone does not, however, extend indefinitely. When the jet solidifies, it becomes unstretchable, and beyond a certain point the diameter of the envelope cone no longer

increases [52] and becomes an envelope cylinder [222]. Mit-uppatham *et al.* [243] noted the dependence between solution concentration and the diameter deposition pattern. The deposition area decreased with increasing concentration due to stabilising viscoelastic forces, which also increased the fibre diameter [243].

Sometimes deposition may form some type of regular patterning. Khil *et al.* [289] have reported that the surface morphology of fibre mat changed with increased deposition time. They noticed spontaneous patterning on the mat when fibres started to accumulate at certain points, yielding higher fibre densities [289]. Polyurethane (PU), for example, has been found to self-align into honeycomb patterns on the collector surface [290]. This phenomenon has been attributed to residual charges on the fibre layer and the electrical properties of the collector [290]. The use of a patterned collector such as wire mesh or grid is, however, an easier and more controllable way to form visible patterns on the electrospun fibre web [224, 291].

2.3 Properties of Electrospun Fibres

Electrospun fibres possess many intriguing properties, which often differ from those of conventional polymeric fibres. This section presents the properties of electrospun fibres and discusses how they can be influenced by varying the process parameters.

The fibre web can be collected as such, but typically fibres are collected as a fibrous coating onto a substrate covering the collector. Usually electrospun fibres form a uniform web consisting of relatively straight, randomly oriented fibres, but also random coiling and looping of electrospun fibres has been observed widely [39, 221-222, 292-293], see examples in Figure 7. Reneker *et al.* [39, 221-222] suggested that the coiled morphology of nanofibres is caused by the looping of the jet. Kessick and Tepper [292] have been able to produce uniform helical structures using a composite solution. The composite consisted of non-conducting polyethylene oxide (PEO) and conducting polymer polyaniline sulphonic acid. They explained that the helical structures were caused by viscoelastic contraction upon partial neutralization of charged fibres [292]. Crimped fibres, the appearance of which resembles the coiled morphology, have also been produced with the aid of air flow [294].

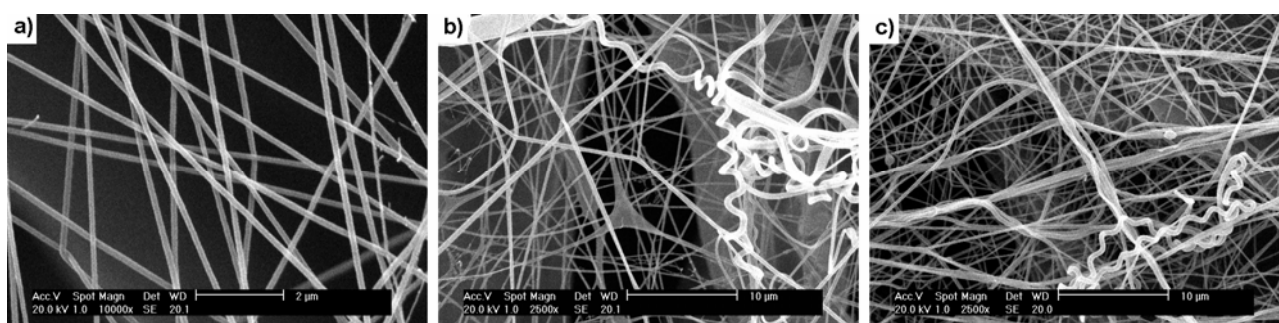


Figure 7. Example pictures of randomly oriented web composed of relatively straight fibres (a) and looping fibres (b & c).

A wide variety of parameters including solution, process and environmental parameters affects the electrospinning process and properties of the forming fibres. Studies to determine the effect of several parameters on the properties of the electrospun fibres such as the morphology and the diameter of the fibre,

have been conducted by several research groups, such as Baumgarten [205] with PAN, Deitzel *et al.* [225] with PEO, Mit-uppatham *et al.* [243] and Supaphol *et al.* [262] with polyamide-6 (PA6), Gupta *et al.* [249] with PMMA, Zhang *et al.* [295] with polyvinyl alcohol (PVA), and Tan *et al.* [280] as well as Cui *et al.* [296] with polylactides. We conducted our parameters study with PA6. The effects of the parameters on fibre diameters and fibre diameter distributions are more fully discussed in Paper VI, but a short review is also included here.

The fibre diameters of the electrospun fibres typically range from some tens to some hundreds of nanometres, but also diameters of less than 10 nm have been achieved. Hou *et al.* [180], for example, obtained bead-free polylactid acid (PLA) fibre of 5 nm, Fong and Reneker [297] measured a diameter of 3 nm from elastomeric fibre between two beads, and Huang *et al.* [217] prepared PA46 nanofibres having diameters of 1.6 nm or less [217]. The theoretical limit for the smallest fibre diameter can be determined by the size of the polymer molecule, which typically is a few tenths of a nanometre. If the smallest coherent fibre contains six or seven polymer chains in its cross-section, the minimum diameter would be around 1.2 nm [217]. Small diameters are preferable when pursuing the largest specific surface area. Huang *et al.* [298] also noticed that fibre web consisting of the finer fibres also exhibited higher tensile modulus and ultimate tensile strength.

Mit-uppatham *et al.* [243] found an exponential dependence between the fibre diameter and the PA6 concentration of the solution, while a power law dependency was found by Gupta *et al.* [249] with PMMA. The nature of the dependency seems to be related to the polymer-solvent system. In the presence of associative interactions such as hydrogen bonding, the increase in the fibre diameter with the increasing polymer concentration has been found to be stronger than expected for the non-associative polymers [264]. Small fibres are obtained at low viscosities, but the low viscosity usually also promotes the formation of beads. In some applications beads can be desired and their controlled preparation has gained some interest [242, 299], however they are often considered as defects to be eliminated [261, 300]. The presence of beads, for example, deteriorates the mechanical performance of fibres [298].

The amount of the chain entanglements discussed earlier (Chapter 2.1) is not the only factor determining the morphology of the formed fibres. Even though occurrence of beads has been typically associated with low viscosity solutions [242, 301], it is also affected by electric field [225, 237, 242, 278, 302-303] as well as solvent system including the mixture ratio of two solvents [304] or volatility of solvent [261]. The change in the bead-fibre morphology can also be induced using additives such as salts [137, 214, 237, 258, 260, 295, 305-306], polyelectrolytes [255], ionic surfactants [261, 300] or some other additives, which may change the properties of the solution, mainly the conductivity [217, 264]. Typically these additives not only reduce the amount of beads, but also reduce the fibre diameters. Increased conductivity of the solution leads to higher net charge density, which suppresses the Rayleigh instability and enhances the whipping instability leading to the formation of bead-free fibres and smaller fibre diameters [300]. The effect of conductivity can also be reversed; for example, salt has also been found to increase the fibre diameter [243, 262, 307], since higher net charge density may also cause higher mass flow. In addition to the above, other solution parameters also affect the fibre diameters and the morphology. These parameters include, for example, the molecular weight

[238, 243, 262, 296, 299, 308-310] and the molecular weight distribution [308] of the polymer, and the surface tension [125, 214, 237, 246, 310], the pH [311] and the temperature [243, 262] of the solution.

As with the conductivity of the solution, the strength of the electric field has also been found to have contradictory effects on fibre diameter. The electric field can be controlled by changing the voltage or the distance. The observed decrease in the diameter with the increasing electric field [126, 147, 225, 258-259, 299, 301, 312-319] can be easily explained by higher electrostatic forces, and the observed increase in the diameter [137, 147, 237, 240, 262, 295, 303, 312-313, 320] with a higher mass flow. Several groups have also reported that the smallest fibres are produced in the middle range voltage or field [205, 281, 296, 314]. Increase in the flow rate usually increases the fibre diameter [137, 240, 258-259, 280, 296, 312, 315] as well as the increase in the nozzle size [260, 305, 320]. Other process parameters affecting the fibre diameters or the fibre morphology include the polarity of the charging voltage [262, 283, 318, 321-322], the gas flow around the jet [323], as well as the ambient temperature [320] and humidity [324-325]. The properties of electrospun web structures may differ from similar structures composed of larger fibres such as spun bond nonwovens. Hong *et al.* [326] noticed that water permeability and water vapour transport properties of electrospun and spun bond webs were different. Zhou *et al.* [87] found that the pressure drop of sub-micron PLA fibre layer was smaller compared to a layer of 10 μm fibres. Small fibre diameters induce a slip-flow effect which accounts for the difference [32, 187]. This is discussed in Chapter 4.2.

The fibre diameter distribution of electrospun fibres can be wide [225, 299, 313, 319, 327] and its width depends on solution and process parameters. Large fibre diameter distributions have been observed, for example, with a high polymer concentration [51, 98, 320, 327], with a high flow rate [260] and a large nozzle [320], with highly volatile solvent [94, 159], and when fillers [328-329] or two different solvents are used simultaneously in the solution [260, 330]. The fibre diameter distribution as well as variation of diameter along the fibre depends on the jetting mode. Smaller variation in fibre diameters and fewer beads were obtained in stable mode than other modes [270]. The applied process also has an influence on the fibre diameter variation. Electrospinning from free surface or from droplets of uncontrolled sizes also leads to larger diameter distribution than using nozzles [218].

In addition to beaded fibres certain other fibre morphologies can also be expected in electrospinning. Flat ribbon-like fibres may be formed if the surface of the jet dries prior to the core thus forming a skin, which collapses into a ribbon-like structure as the solvent evaporates from the core [159, 215, 220, 239]. This is often observed with highly concentrated solutions [238]. The surface porosity of electrospun fibres has been observed and studied by several groups [259, 331-332]. The amount, diameter, shape and distribution of the pores depend, for example, on the humidity of the surrounding air [332] and the volatility of the solvent [259, 331]. Bognitzki [331] attributed this characteristic of electrospun fibres to the volatility of the solvent and the phase separation in the jet. Smaller fibre structures between the main nanofibres forming a continuous web have also been found [Paper VI, 324, 333]. Ding *et al.* [324] refer to such structures as nanowebs, and they noticed that the occurrence of these nanowebs was related to certain conditions such as high voltage, low relative humidity and fast phase separation within the forming fibre. Holzmeister *et al.* [333] noted that

this is characteristic of polyamides, in particular concentrations, but the origin of the phenomenon is not known. Globule-like artefacts have been found on the surface of fibres prepared with solutions containing salt [Paper VI, 295], and Zhang *et al.* [295] considered these small particles to be salt crystals on the surface of the fibres electrospun from a solution containing this salt.

The electrospinning process itself and the process parameters may affect the properties of the polymer, for example, its internal structure. Changes have been observed in crystalline structure [239, 334-338] and the degree of crystallinity of the polymer [286, 299, 339]. The crystalline structure of polymorphic PA6 polymer, for example, changes from α -form to γ -form during electrospinning [239, 334-336]. The necessary time for crystallization of the α -form is longer than that provided in electrospinning, leading to γ -conformation, which has also been observed in melt spinning with high take-up speeds [335]. The short formation time also affects the degree of crystallization. Deitzel *et al.* [286] have noticed that the crystalline structure of electrospun PEO fibres was poorly developed. The crystallinity of poly- ϵ -caprolactone (PCL) [299] and poly-L-lactide (PLLA) [339] were also lowered in electrospinning. It was found that the degree of molecular orientation in fibre may be affected by varying the electrospinning parameters [339].

The molecular orientation in electrospun fibres was also observed by Bellan *et al.* [340], who have studied the mechanical properties of electrospun fibres with atomic force microscope (AFM). They found that Young's modulus for the PEO nanofibres was larger compared to thin films and bulk material. The orientation explains the better mechanical properties of nanofibres compared to bulk [340]. Others have also observed the improved mechanical properties of the nanofibres compared to those of larger objects of the same material. Tsai *et al.* [46], for example, have reported that the areal mass-normalized strength of electrospun nanofibre fabrics can be ten times higher than that of melt-blown microfibre fabric of same material. Higher molecular weight has found to enhance the physical properties such as thermal stability and the stress-strain properties of PVA nanofabric [301]. The use of branched polymer instead of linear lowered the Young's modulus and increased the straining capacity of poly(urethane urea) electrospun membrane [250]. The use of higher voltages with polyacrylic acid (PAA) resulted in fibres with a larger heat capacity in the glass transition region [240]. In addition to these kinds of changes, the properties of electrospun fibres can be modified on a larger scale using additives and fillers to form composite fibres. Such modifications and composites are discussed in Chapter 3.

2.4 Electrospinning Designs

Electrospun fibres can be prepared using a variety of designs. The properties of electrospun fibres and the web can also be varied by modifying the equipment. The status of the current technology and advances in electrospinning systems are reviewed below. Multi-nozzle electrospinning design for large scale production is discussed more thoroughly in Chapter 4.1.

Usually the electrospinning designs producing randomly oriented nanofibre webs utilize some kind of nozzle, even though jetting can also occur from the free surface of the polymer solution. Descriptions of these nozzleless spinning designs can be found throughout the history of electrospinning from the early patents

[89-90, 192] to the newly introduced designs [35]. Kessick and Tepper [341] have reported one kind of micro-scale electrospinning event involving the formation of a nanofibre interconnection between two droplets having a size and distance on a micrometer scale. Nanofibre interconnection was formed with the aid of charged electrodes between neutral droplets, and spontaneously between oppositely charged droplets [341]. Lukas and Torres [342] described a design where a polymer solution drop was laid on top of a steel rod electrode, which was connected to a voltage source. A grounded collector was located above this electrode. Small conical protrusions of polymer solution appeared when the voltage was applied. Multiple jetting was observed from the droplet, which increased the productivity, but the appearance of multiple jets was sensitive to distance. The amount of jets and the separate deposition areas as well as shape of depositions was also dependent on the size of the droplet, the concentration of the polymer solution and the voltage [342]. The productivity of electrospinning from the free solution surface can be multi-fold compared to the nozzle design. Productivity of the nozzle design can be increased by scaling-up by using multiple nozzles. This approach is discussed in greater detail in Chapter 4.1.

Yarin and Zussman [343] have reported experiments utilizing upward nozzleless electrospinning from a solution surface having magnetic fluid below the spinning solution layer. The magnetic field caused perturbations which appeared in the form of conical spikes on the surface of the magnetic fluid. These perturbations acted as electrospinning sites when voltage was applied. The jet density on the surface of the magnetic fluid system was high, 26 jets/cm² being 12-fold compared to the operational limit with nozzle lattice (2.25 jets/cm²) [343]. The productivity of the electrospinning was also enhanced by Dosunmu *et al.* [218], who used a porous tubular surface, having a pore size of 10 µm - 100 µm, as an emitting electrode. They obtained a vast amount of jets yielding up to 250-fold productivity compared to a single-nozzle design. The increase in productivity was partly due to the larger fibre diameter, but it was mostly caused by the greater number of jets. The number of jets varied over time; when one jet dried up another one emerged. Even though the mean diameter of fibres was similar in both cases, the diameter distribution was broader in the case of porous tube. This was caused firstly by the size distribution of the drops on the tube surfaces from which jets were emerging, and secondly by the differences in the geometry of the electric field between the tube and a hollow capillary nozzle [218].

In the design described by Simm *et al.* [89-90], the emitting electrode was an annular spinning wheel. The wheel had cogging on its perimeter and was partly immersed in the solution. The clogged, rotating wheel carried the solution to the spinning zone, but the cogging also had sharp points where field intensity was higher and therefore jetting was elevated [89-90]. This design was further improved by Jirsak *et al.* [35] by widening a thin spinning wheel to the shape of a rotating cylinder, which increased the fibre forming surface and enhanced production. The circumference of the cylinder was fitted with lugs and/or recesses to ensure a large amount of solution on the surface from which jetting could occur [35].

The basic construction of nozzle-based electrospinning equipment is simple but different kinds of features have been introduced. Variations have also been made to the nozzle-based electrospinning designs in order to enhance the process or to modify it so that certain special structures or properties can be gained for the

forming product. A typical nozzle-based electrospinning set-up is static, but some dynamicity can be applied. Rotating emitter designs have been reported by several groups [24, 27, 344-346]. In these designs rotation improves the evenness and spreading of the nanofibre web. Patents by Donaldson Company [24, 27] described an emitter consisting of a rotating union with offset holes around its periphery facing the collector. A similar nozzle design is presented by Kim and Park [344], but besides holes they also introduced capillary nozzles onto rotating emitters. Chang *et al.* [346] combined a rotating nozzle design with a moving outlet.

Dubson and Bar [347] suggested that the strength of the electrospun nonwoven material may be enhanced with dynamic altering of the electric field. They used stationary or rotating auxiliary electrodes that affected the electric field in order to generate twisted, inhomogeneous fibre bundles [347]. Dynamic field has also been utilized in a field-controllable collector electrode generating an AC (alternating current) electric field in order to control fibre deposition [285]. Typically electrospinning and spraying are conducted using DC potential, but AC potentials can also be used as spinning voltage [348]. AC voltage was reported to be more efficient in electrospraying when the substrate was insulating because substrate does not accumulate charge in an AC system. In electrospinning a significant difference between AC and DC potentials was the amount of whipping instability. Whipping was reduced and eliminated with AC potential, leading to increased fibre diameter [348]. Vibration technology has been applied to the process by He *et al.* [244, 349] in order to reduce the viscosity of the solution or melt. The lower viscosity enabled the use of lower voltage and the formation of smaller fibres compared to the same conditions without the vibration [244, 349]. Air flow can be used to aid the electrospinning process [350-351], and gas flow to stabilize the Taylor cone [323]. Air flow inside a confined space can also be used for production of crimped electrospun nanofibres [294].

The electrospinning set-up can be directed either horizontally or vertically. Most laboratory scale devices are arranged downwards or horizontally. The advantage of upward electrospinning is the reduced dripping of the solution on the substrate. Bottom-up electrospinning has occasionally been presented, for example, by Lukas and Torres in laboratory scale from droplet [342] and on a larger scale by Kim and Park [351]. In larger scale bottom-up equipment [351] the excess solution was collected using overflow collection nozzles. Joe and Zhou [352] have reported the effect of the spinning direction of melt-electrospinning. In the vertical set-ups the downward electrospinning produced more than 10 times larger fibres than the upward set-up. The fibre diameter of the horizontal set-up was between the previous two [352].

Use of a controlled atmosphere may also have advantages. An electrospinning chamber with a controlled atmosphere (temperature, pressure and composition of the gaseous environment) can improve the quality of electrospun fibres. The smaller diameter and smaller diameter distribution of fibres can be obtained since higher voltages can be used, and the reduced drying rate of fibres enables greater stretching [353-354]. Controlling humidity and temperature of the spinning atmosphere can also be crucial, for example, when polymer solutions can interact with moisture [259, 332]. The apparatus for elevated temperature electrospinning enables not only melt-electrospinning but also the electrospinning of solutions which are not dissolvable in acceptable solvents at room temperature [352]. Nu [355] has presented electrospinning equipment capable of reactive electrospinning. The electrospinning process was coupled with a closed in-

line reactor for chemical or photochemical reactions such as cross-linking [355]. Portable electrospinning equipment to be used at the application site has been introduced by Dubson and Bar [356].

Use of polymer blends is discussed in Chapter 3.1, but nanofibre mat consisting of two polymers can be prepared using separate nozzles or specific nozzles for two solutions. These approaches also enable the use of polymers that do not have a common solvent, which makes the blending of polymers into the same solution impossible. Tsai and Schreuder-Gibson [57-58] have electrospun different polymers from two adjacent nozzles. They observed distortion of the deposition patterns and poor mingling of fibres [57-58]. Ding *et al.* [357], for example, have demonstrated preparation of PVA/cellulose acetate (CA) blend fibre mat with uniform properties using a multi-nozzle design. Bi-component fibres have been prepared by Gupta and Wilkes [358-359] by attaching two capillary nozzles together. They obtained a mat composing of side-by-side bi-component fibres [358-359]. However, a more common method for preparation of bicomponent fibres is the use of a co-axial electrospinning [241, 360-367], which produces core-shell structured fibres. Tri-axial nozzles have been used in coaxial electrospinning to provide additional sheath flow of solvent around the co-axial jet in order to prevent solidification of the polymer solution in the nozzle [241].

The electrospinning designs, and typically the collection system, can be modified for the preparation of different fibre assemblies such as controlled deposition, aligned or specially patterned fibre mesh and 3D structures [37]. Electrospun nanofibres may be aligned with different techniques. Precise deposition and alignment of nanofibres to be used in nanofibre-based electronics have been prepared using a micro-fabricated scanning tip as an electrospinning source [166]. Sun *et al.* [368] have presented a method called near field electrospinning (NFES) having a minimum distance of 500 μm and capable of controlled deposition of electrospun fibres. The whipping of the jet can be suppressed and thus the deposition area diminished and sharpened by auxiliary electrodes around the nozzle [127, 284-285] or around the jet [286]. Kim [285] was able to produce writing with his design, combining the auxiliary electrode and the field-controllable collector electrode. A precise deposition system was also presented by Greenhalgh *et al.* [369] whose moving nozzle system included both side-to-side and longitudinal movement.

Use of a rotating cylinder as a collector affects the orientation of the fibres [52, 279, 370-371]. When fibres are collected in this way, the packing density of the fibres is increased and thus the porosity of the web is decreased [52]. With an additional guide electrode and sideways movement of such a cylinder, a single fibre can be collected around the cylinder [370]. Aligned nanofibre strings can be achieved by collecting nanofibres with sufficient speed onto the sharp edge of the rotating disc [372] and local alignment can also be obtained onto the planar surface of the rotating disc as a collector [373]. Another approach for production of aligned fibres is the use of a collector that consists of two pieces separated by a gap. Due to the electrostatic interactions, the nanofibres form a parallel array across the gap [374-377]. The use of a rotating drum collector consisting of wires combines the two methods, rotation and the gaps between the wires, which enhance the alignment [378]. The rotating collector can also be used in order to dip, for example, electrospun cellulose fibre into a coagulation bath [379].

Yarns consisting of electrospun fibres can be prepared, for example, by twisting aligned fibres into yarns [279, 380], combining fibres from two oppositely charged fibres into yarns [381], as well as producing fibre mesh onto the surface of a liquid bath and collecting fibres continuously from the interface [382] or through the liquid bath [383]. The method for the preparation of continuous twister electrospun yarn has already been described by Formhals in the 1940s [201] and with a novel design [14] such yarns can be continuously collected with a speed of 70 m/min.

Tubular 3D products with circumferentially aligned fibres are obtained with a rotating drum, and additional electrodes can be used to guide fibres enabling the diagonal alignment of fibres in these tubular products [371]. Mitchell and Sanders [384] have presented controllable electrospinning equipment where the atmospheric and process variables can be controlled. Another speciality of their design is the collector, which is located between the two charged electrodes and attached to the x-y-z translation stage. The equipment provides more efficient control of the fibre diameter and inter-fibre spacing than conventional designs. The authors also claim that their design, having a collector independent from the electrodes and controllable during electrospinning, will enable the development of variable architecture with complex 3D shapes in the future [384].

2.5 Models of the Electrospinning Process

Electrospinning is an interesting and complex process. It is, therefore, hardly surprising that modelling has been used to gain a better understanding of the fibre forming event. The present section contains an overview of the models employed.

Modelling of the electrospinning process has been mainly concerned with the electrically driven polymer jet and its instabilities. Reneker *et al.* [39] and Yarin *et al.* [40] calculated the looping paths of the whipping jets, and found a reasonable correlation with experimental data. Yarin *et al.* [211] also studied the Taylor cone and jetting from it, and presented a theoretical model explaining how the shape of the droplet on the tip of the nozzle is affected by the electric field. A steady state jet of the electrospinning was modelled by Spivak *et al.* [210], while Russell *et al.* [45] described the fundamental physics and fluid dynamics relevant to the instabilities at the polymer interfaces. Hohman *et al.* [41-42] have made an electrohydrodynamic model for the Newtonian jets in order to develop a theoretical framework for understanding the physical mechanics of the electrospinning process. They studied the stability of the charged jet in the electric field, and determined how properties, such as charge density, vary along the jet. Feng [385-386] as well as Carroll and Joo [387] have modelled jets of both Newtonian and non-Newtonian solutions. Their models were used to study the behaviour and the phenomena of the jet, for example, the effects of the extension thinning and thickening, and the strain hardening on the polymer jet [385].

In addition, Fridrikh *et al.* [274, 388] have studied the fibre diameter. They modelled the charged jet and determined the jet diameter as a function of surface tension, flow rate and electric current [388]. Lu *et al.* [256] devised a computer simulation to study the effect of the solvent, focussing on the energy change in the process of molecule orientation. He and Wan [389] have proposed a theoretical model for the electric

phenomena of electrospinning, and obtained an allometric scaling relation between the current of the charged jet and the voltage. Reneker *et al.* [222] have prepared a computer model which calculates the predicted path of the jet from seventeen input quantities. The input quantities included solution parameters such as concentration, viscosity, relaxation time and density of the solution, process parameters such as distance and voltage, as well as the ambient parameters such as temperature and relative humidity. Another model utilizing thirteen input parameters in the prediction of the fibre diameter have also been reported by researchers from the University of Akron [223].

In addition to the whipping jet, another interesting object for modelling is the electric field of the different kinds of electrospinning set-up. The shape of the electric field depends on the geometry of the electrospinning equipment in terms of the shapes of the electrodes and the distance between them. Electric fields can be presented simply as 2D field vector images, examples of which can be seen in Figure 5 on page 15. In these images the vectors illustrate the direction of the overall electric field. The magnitude of the electric field can be expressed to some extent by means of the density or the length of the field lines, but the exact values cannot be presented. These kinds of electric field plot have been presented for different kinds of single-nozzle designs. Deitzel *et al.* [286], for example, illustrated a plain design of a nozzle and a collector and the same design with auxiliary electrodes, Li *et al.* [374] illustrated a design where aligned electrospun fibres were collected between two parallel electrodes and Theron *et al.* [372] a design where aligned fibres were collected onto the edge of the rotating disc. Another approach for presenting the 2D electric field is that of Furlan *et al.* [390] who presented the electric field in the vicinity of the electrodes as equipotential lines. They also used the field line presentations to illustrate the entire electrode design with different potentials.

Fang *et al.* [391-392] have made a 2D model of the electric field of their electrospinning nozzle design in order to examine different electrode configurations and the use of auxiliary electrodes between the nozzles. One of their targets was to reduce the interference between jets from different nozzles. They utilized the model and its results to build a multi-nozzle electrospinning design [391-392]. Another approach to multi-jet modelling has been adopted by Theron *et al.* [393] who studied the interactions between the jets. They presented their results as top and side views of the predicted paths of the jets. They noticed that adjacent jets having the same polarity were pushed away from each other, and that the vicinity of the other jets also changed the shape and size of the deposition pattern. When jets were arranged, for example, in a row, the envelope cones of the inner jets were squeezed from the sides, leading to elliptical deposition [393].

The multi-jet electrospinning design was also modelled by Kim *et al.* [284] for stability analysis and comparison of multi-jet and single-jet designs. The comparison was made using an electric field concentration factor (EFCF). The determination of EFCF included a brief study of the directional field components, and it expressed whether the electric field is diverging towards outside areas or converging to the spinning axis. EFCF value was positive near the nozzle and became negative in the proximity of the collector. They observed that the motion of the jet from the central nozzle of the multi-jet system may be completely the same as the motion of the jet from a single nozzle. They also demonstrated by modelling and

experimentally that the cylindrical auxiliary electrode around the nozzle stabilized the jet and contracted the deposition area. Group presented this EFCF in the form of line charts and 3D colour plots [284].

In Paper IV we have used another approach and paid more attention to the individual field components. We present the overall field strength as 2D colour plots, but the individual field components are presented as line charts to illustrate the shape of the electric field and how it affects the jet in different parts of the electric field. The models were prepared from a one-nozzle design [Paper IV, 288] and multi-nozzle design [288] as described in Chapter 7.1.

3 Nanostructured Fibre Composites

A wide range of polymers are applicable in electrospinning. Solution electrospinning is applicable to polymers that are soluble in common solvents under normal conditions. Electrospinning has been applied to polymers that are commonly used in many plastic products (see Table 1). These polymers include commodity plastics such as PS, polyvinyl chloride (PVC) and engineering plastics such as polyamides, polyesters and polyimides. Water soluble polymers such as PVA and PEO are also very widely used in laboratory trials and as a model material due to their unharmed properties. Electrospinning has also been applied to natural materials and chemically modified natural materials [251] such as cellulose derivatives and proteins. Melt-electrospinning, on the other hand, can be applied to polymers whose melting temperature is sufficiently low such as polyesters [394], but it also allows the use of polymers whose dissolution is problematic or unfeasible, such as PE and PP [206-208].

Table 1. *Examples of the polymers applied in electrospinning with literature references and information on the special features of the polymer and/or the examples of the application fields.*

Material	References	Features/ applications
Commodity plastics		
Polyethylene (PE)	206-208, 395	Usually melt, but also solution electrospinning
Polypropylene (PP)	206-208	Melt-electrospinning
Polystyrene (PS)	57, 62, 78-79, 129, 155, 183, 215, 242, 248, 257-258, 277, 300, 332, 396-397	Hydrophobic, typically exhibit surface porosity when electrospun. Filtration, matrix in composite materials, model material etc.
Polyvinyl chloride (PVC)	69, 159, 263, 398-399	Filtration etc.
Engineering and specialty plastics		
Polyamides (PA)	27, 30, 34, 57, 59-60, 63-67, 98, 105, 165, 170, 180, 217, 243, 262, 313, 321-322, 326, 333, 335-337, 367, 400-403	Filtration, reinforcement, matrix in composite materials, model material etc.
Polyacrylonitrile (PAN)	24, 48, 51-52, 57, 62, 64, 68-70, 205, 279, 283, 307, 364, 366, 377, 404-411	Filtration, precursor for CNF, matrix in composite materials etc.
Polyaniline (PANI)	6, 159-165	Conductive polymer.
Polybenzimidazole (PBI)	59, 63, 412-413	Filtration, precursor for CNF
Polycaprolactone (PCL)	57, 121, 127-128, 260, 299, 317, 330, 371	Biodegradable polymer.
Polycarbonate (PC)	56-57, 59, 86, 302, 304, 397, 414-415	Filtration etc.
Polyethylene oxide (PEO)	5, 56-57, 67, 159, 163, 237, 255, 286, 318, 328, 325, 340, 416	Water soluble. Model material, filtration etc.
Polyesters	6, 159, 289, 326, 329, 394, 417	Model material, matrix in composite materials etc.
Polyfluorostyrene	184	Hydrophobic.
Polyimides	6, 88, 418	High strength. Filtration etc.
Poly lactides	87, 121, 130, 137, 139, 180-182, 260, 280, 306, 314, 339, 362, 419-421	Biodegradable polymer. Medical applications, removable templates, filtration etc.
Polymethyl methacrylate (PMMA)	174, 303, 364-366, 397, 422-424	Removable core, matrix for composite materials etc.
Polyphenylene vinylene	147	Conducting.
Fluoropolymers (e.g. Kevlar)	6, 84-85, 425	Filtration, high temperature applications etc.
Polypyrrole (PPy)	167, 365	Conducting. Precursor for CNF etc.
Polysulphones	72, 82-83	Filtration.

Material	References	Features/ applications
Polyurethanes (PU)	34, 56-57, 59, 61, 63, 71-72, 250, 290, 315, 327, 367, 396, 398, 426-427	Filtration, matrix for composite materials, applications where elasticity is needed, protective clothing, etc.
Polyvinyl alcohol (PVA)	67, 73-77, 158-159, 238, 263, 295, 301, 308-309, 316, 416, 428-430	Water soluble. Model material, filtration, precursor for CNF, carrier polymer for conductive polymers etc.
Polyvinyl pyrrolidone (PVP)	135, 145, 293, 362, 419, 431-433	Water soluble. Carrier polymer for nanoparticles, removable core, wound dressing etc.
Polyvinylidene fluoride	169, 215, 338	Piezo-, pyro- and ferroelectric polymer
Synthetic rubber	434	
Natural and chemically modified natural materials		
Cellulose, its derivatives and lignin	69, 80-81, 84, 142, 241, 311, 320, 357, 379, 435-436	Filtration, precursor for CNF, drug release etc.
Chitosan	251-253, 437-438	Antimicrobial. Medical applications etc.
DNA	6, 122	
Petroleum derived pitch	439-442	Precursor for CNF
Silk	443-444	
Proteins (e.g. collagen and fibrinogen)	119-120, 157, 251, 298, 319, 445-446	Medical applications such as drug delivery and tissue engineering

The application field of the electrospinning is not limited to purely polymeric materials, and the diversity of the materials can be increased, for example, by using functional polymers and their blends, using inorganic or polymeric composites, and encapsulation of functional additives inside the electrospun nanofibres [18]. One interesting field is the use of nano-sized particles with different shapes as filler [50]. Another field is preparation of ceramic nanofibres from metal containing composite nanofibres by pyrolyzation [15]. More variations and applications are possible by functionalization and modification treatments of electrospun fibres. Xu [355] has introduced electrospinning equipment with in-line reactor for chemical and photochemical reactions, and Gupta *et al.* [447] have demonstrated simultaneous cross-linking and electrospinning of photo-cross-linkable polymers. Nonetheless, functionalization and modification of electrospun fibres is typically conducted as a subsequent, separate process step. This kind of modification can include, for example, cross-linking treatments [61, 76, 316, 417, 428, 446, 448]; functionalization of fibre surface with active species [134, 216, 449]; coating of nanofibre, for example, by dipping it into chemical bath [450-451] or using a chemical vapour deposition (CVD) method [178, 180, 452]; and surface modification of electrospun fibres with plasma [46, 453]. Furthermore, one intriguing method utilizing electrospinning is the production of carbon nanofibres (CNF) by carbonization of electrospun precursor fibres of different materials such as PAN [172, 349, 404-408, 454-455] and petroleum derived pitch [439-442], as well as composites containing catalytic fillers [149-151] or carbon nanotubes (CNT) [107, 349, 454-456].

This chapter reviews the preparation of the nanofibre composites from polymer blends and co-polymers in Chapter 3.1, and the use of different kinds of nanofiller in electrospun composite fibres in Chapter 3.2.

3.1 Polymeric Blends and Co-Polymers

Nanofibres composed of polymer blends can be achieved using different methods, for example, by preparing bi-component fibres with a core-shell or a side-by-side structure, mixing of two polymers, and using co-

polymers. Polymeric blends can be used in order to impart specific properties, structures, or functionalities in the nanofibres. Other common situations for the use of polymeric blends are cases where one polymer component is poorly or non-electrospinnable. The other polymer is used as a carrier polymer, which enhances or enables the fibre formation in the electrospinning process by increasing the amount of the polymer chain entanglements within the solution.

Core-shell structured bi-component fibres can be achieved using subsequent coating of electrospun fibres [181-182, 364, 452], but bi-component fibres with two clearly distinct parts can also be prepared as a one-step process from two liquids using a side-by-side approach [358-359] or a co-axial, two-capillary nozzle [360-367]. Core-shell structured fibres obtained with coaxial electrospinning can enhance material properties, for example, in many medical applications [362-363], but their preparation is not as easy and straightforward as in normal electrospinning. The ratio of the flow rates of the two components is critical. If the flow rate of the core solution is too high, it might protrude through the shell, and form arch-like bulges on fibres [364]. The evaporation of the core solvent might cause porosity of the shell [364]. If the coaxial electrospinning or the coating of electrospun nanofibres is followed by the selective removal of the cores, the method can be used to produce tubular, hollow nanofibres [182, 360, 365]. The use of the side-by-side approach enables preparation of the bi-component fibre mat that possesses the properties of both of its components [359].

Blending of polymers into the same solution or into the same web can be used to control different properties of the electrospun nanofibres. The mechanical properties of electrospun fibres have been adjusted by using various mixing ratios of PU/PVC [398]. However, the mechanical strength of the bicomponent electrospun PVA/CA web, prepared using multi-jet electrospinning was determined by the ratio of PVA/CA in the blends [357]. Polyethylene glycole (PEG) has been added to electrospun PLLA fibres in order to modulate the hydrophilicity and, thus, the biocompatibility of the nanofibres to be used as a material for tissue engineering scaffolds [132]. A blend of PEG and CA has been used to form thermo-regulating ultra fine fibres, where PEG moieties trapped inside the CA matrix act as phase change material (PCM) [457]. Surface porosity, whose formation is related to evaporation of the solvent, is sometimes naturally obtained on the electrospun fibres [259, 331-332], but polymer blends can be used to obtain a porous structure with pores extending to the fibre core. A microphase-separated structure can be prepared by blending two immiscible polymers into the co-solvent for electrospinning [160, 409, 415, 419, 458-459]. The selective removal of one component from the electrospun fibres leads to a fibrous structure with interconnected nanoporous network having dimensions of tens of nanometres throughout the fibre surface and interior. The solvent evaporation rate and the differences in the solubility of the components in common solvents affect the phase separation process and, thus, results in the intriguing morphologies [415]. Bognitzki *et al.* [419], for example, blended PLA and polyvinyl pyrrolidone (PVP) polymers in order to make fibres with nano-scaled morphologies. The phase separation occurred during the fibre formation, which led to highly structured co-continuous phase morphology. PVP was removed in a subsequent process and porous PLA fibres with specific surface topologies were obtained [419]. Peng *et al.* [459] blended PAN with co-polymer of AN and MMA. After oxidation and carbonization, a CNF structure was obtained with interconnected nanoporous network having

dimensions of tens of nanometres throughout its surface and interior [459]. Wei *et al.* [397, 415] have reported the spontaneous formation of core/shell structures from polymer blends due to the phase separation of components having different rheological properties.

Nanoporous structure with more organised structure can be obtained using self-organising co-polymer materials. Self-organization is a phenomenon which appears with many natural polymers, but it can be also obtained with synthetic block-co-polymers [460]. The structural order can be created in the presence of hydrophobic and hydrophilic effects, hydrogen bonding, columbic interactions, and van der Waals forces [460]. The morphology of block-co-polymer can be controlled by varying the number of blocks, their lengths, and their chemical composition [461]. Possible structures are, for example, cubic arrays of spheres, hexagonal arrays of cylinders, bi-continuous cubic phases or lamellae [461]. Electrospinning of self-organization materials has been infrequently reported. Electrospun block-co-polymer fibres with irregular phase separated structure have been observed by Fong *et al.* [297] using a styrene-butadiene-styrene system, and with more ordered structure by Kalra *et al.* [462] using poly(styrene-block-isoprene). However, most of the publications [463-466] concern the same research as described in Paper I.

Co-polymers are also used in the preparation of nanofibres with specific properties. Styrene-butadiene-styrene tri-block-co-polymer has been used for elastic nanofibres [297]. Poly(methyl methacrylate-co-tetrahydroperfluoro octylacrylate) has been used to obtain specific fluorinated surface chemistry on electrospun fibres [467]. Sulfonicated poly(ethylene-co-vinyl alcohol) has good electro-activity and may have applications, for example, as a self-doped polymer electrolyte membrane and an artificial muscle [468]. Electrospun biodegradable poly(butylene succinate-co-butylene adipate) fibres have been suggested as being suitable for filters and for serving as a reinforcing component in the composite systems [104]. Many medical applications of electrospun fibre such as tissue engineering and drug release materials also utilize biodegradable co-polymers [122-126, 139-140, 469], since the degradation rate of such co-polymers can be varied by adjusting the ratio of the fractions in the co-polymer composition [125]. Controlled release materials can also utilize non-degradable co-polymers. Methacrylate-based co-polymers with different structures, for example, are able to release their fillers at different pH levels in aqueous media [303]. Sanders *et al.* [138] have prepared poly(ethylene-co-vinyl acetate) fibres containing aqueous reservoirs which will eventually burst and thus release their content due to osmotic swelling.

Auxiliary carrier polymers have been used, for example, in the preparation of conductive nanofibres from intrinsically conductive polymers. Electrospinning of pure polyaniline (PANI) is reported by MacDiarmid *et al.* [161], but typically the molecular weight of the intrinsically conducting polymers is relatively low, which complicates their use in electrospinning. Conduction of electrospun fibre web can be achieved by polymerizing PANi onto surfaces of electrospun nanofibres [470], but typically PANi and polypyrrole (PPy) are blended with non-conductive, higher molecular weight polymers, which serve as a carrier in electrospinning [159-167]. The chain conformation of some polymers can be contracted or rigid (see Chapter 2.1), which obstructs gaining a sufficient amount of chain entanglements for electrospinning even though their molecular weight might be high. The chain conformation of a charged polyelectrolyte, for

example, depends on interactions between the charged polymer and its counter ions in solution [240]. Electrospinnability of polyelectrolytes, such as positively charged chitosan and negatively charged PAA, can be enhanced using ionic additives [240, 254] or they can be blended with other polymers [251, 438]. Electrospinning of pure chitosan, for example, has proven difficult even in the presence of cationic surfactant [251], but fibre formation has been successful when blended with PVA or PEO [251-252, 437-438]. Some polymers have an inherently rigid chain structure, which reduces the amount of chain entanglement in solution. Kim *et al.* [471] blended PAN having a flexible chain structure with rigid polyamic acid in order to reduce the viscosity, and thus enhance the electrospinnability of the solution.

3.2 Composite Fibres using Nanofillers

Nanofillers can be used in order to achieve many properties in electrospun fibres. Spherical nanoparticles of all dimensions in the nano-size range are typically used for their functionalities. Tubular and lamellar nanofillers having one or two larger dimensions are typically used in order to modify the mechanical properties of electrospun fibres. In practice, however, this distinction is not so strict, and particular filler may have several purposes and influence different properties of electrospun fibres. The challenge is to disperse the nanofiller uniformly into the solution and into the fibres, since the presence of the filler agglomerates reduces the bonding area between the filler and the matrix, and may degrade the properties of the fibres [414, 423]. The electrospinning process may also be adversely affected by oversized agglomerates. Deitzel *et al.* [275] have pointed out that the nanofiller should be well dispersed and the filler size should not exceed the initial diameter of the jet if the filler is to be evenly distributed within the formed fibres.

Kim *et al.* [50] have studied the preparation of nanocomposite nanofibres containing one-, two- and three-dimensional nanofillers. They noticed that the nanocomposite can be either a binary or tertiary system consisting purely of the matrix and the filler, or also have nanopores as a third phase. Nanofiller as well as nanopores can act as effective stress concentrators during the mechanical deformation process leading to the brittle-to-ductile transition, and therefore improving the toughness of the nanocomposite. The chain entanglement density in the electrospun fibres might be reduced compared to the nanocomposite bulk due to the high stretch and the aligning of chains occurring during the spinning. This also toughens the material further, since the chains can slip against each other and thus suppress the craze mechanism. [50]

The preparation of electrospun composites with lamellar nanoparticles is discussed in Chapter 3.2.1, with tubular nanoparticles in Chapter 3.2.2 and with spherical nanoparticles in Chapter 3.2.3.

3.2.1 Composites with Lamellar Nanoparticles

Layered silicate clays are typical lamellar nanofillers used in polymeric composite materials [50, 239, 328, 337, 401, 420, 422, 427, 430], but also other lamellar particles have been used in electrospinning. Preparation of a polymer composite containing layered Mg-Al double hydroxide has been reported [472] and also graphite, consisting of one-atom-thick layers of carbon has been used as filler when exfoliated into separate thin nanoplatelets [473]. Lamellar nanoparticles are typically used in order to increase the modulus and strength of the composites [401, 420, 473-474]. Nano-sized clay has also been found to have an effect

on the other properties such as crystallinity [239, 401, 420, 474] and biodegradability of the compound material [420]. Nano-sized clays applied in electrospinning include montmorillonite (MMT) [Paper II, 50, 239, 337, 401, 420, 422, 427, 464] and laponite [328, 430]. Typical particle size of the dry clay particles is in the micrometer range and they are forming layered structures. These dry particles, however, may contain several thousands of individual platelets, which may be well exfoliated and intercalated in optimum circumstances [401]. Achievement of the full intercalation of the layers and the uniform dispersion of the clay particles in the electrospinning solution and in nanofibres is, nonetheless, very challenging. Surface modification of the clay particles [50, 328, 401, 422, 427] may improve their miscibility with the solvent and the polymer.

Daga *et al.* [328] found that the clay-containing solutions led to the larger average fibre diameters than solutions of the neat polymer of the same viscosity. Zhou *et al.* [420], on the other hand, have noticed that the addition of nanoclay may also decrease the fibre diameter compared to the neat polymer fibres of the same polymer concentration, since the clay can act as a charge carrier in solution. A similar observation was made by Hong *et al.* [427] who found a linear dependence between the amount of organically modified MMT and the conductivity of the solution. The presence of clay can also lead to a broader fibre diameter distribution and induce surface roughness [328].

Kim *et al.* [50, 422] noticed that Na-MMT silicates were not exfoliated uniformly in the PMMA matrix, but rather formed intercalated tactoids in the inner parts of the fibres. The used composite was synthesized polymerizing MMA in the presence of Na-MMT [422]. Electrospun fibres with nano-scale dispersion of MMT, on the other hand, have been obtained using solutions prepared from initially melt-processed polymer/MMT composites [239, 401], while solution blending of, for example, PA6 and MMT produced an unintercalated nanocomposite [239]. In addition to the good exfoliation of modified MMT, it has also been found to be oriented along the fibre direction [239, 401, 427]. The balance of the interfacial interactions between the silicate and the surrounding medium seems to be crucial. Fong *et al.* [239] observed that while MMT remained dispersed in a PA6/hexafluoropropanol solution, only a relatively small addition of dimethylformamide to this solution disturbed the chemical balance and led to the agglomeration of the silicate.

Zhou *et al.* [420] used different methods for mixing nanoclay in polymer solution. Firstly they used a premixed compound which was dissolved into solvent, and secondly they dispersed nanoclay particles into the solvent prior to dissolution of polymer. They found that the intercalation was preserved during electrospinning and the clay layers were aligned along the fibre axis regardless of the mixing method. The effect of the mixing methods was seen, however, in the mechanical properties of fibres. Improvement in mechanical properties was obtained with the premixed composite, while the properties of the solution blended composite were not changed significantly from those of the neat polymer. A certain amount of premixed nanoclay increased the crystallinity of the electrospun PLA fibres. In contrast a higher amount of it and the use of the blending method decreased it. The crystallinity of electrospun fibres was also higher

compared to cast film. Due to the effect on crystallinity the increment of the nanoclay thus also affected the degradation rate of the polymer. [420]

3.2.2 Composites with Nanotubes

CNTs are widely used as filler in electrospun fibres [50, 99, 107, 115, 152, 169-170, 329, 349, 396, 410, 414, 416, 423, 454-456, 475-480]. They are typically used as reinforcement components [329, 349, 396, 476-477], but CNTs can also be used to modify the electrical properties of fibres [169-171]. One interesting application of the electrospun CNT-based composite fibres might be piezoelectric strain sensors for smart fabrics [115]. The smallest possible single-walled carbon nanotubes (SWNT) have diameters of 0.4 nm [481], while diameters of multi-walled carbon nanotubes (MWNT) depend on the number of wall layers (0.34 nm each), and may vary from 2 nm to 50 nm [449]. Vapour grown CNTs can have even larger diameters of some hundreds of nm [423]. Other tubular or fibrillar nanoparticles can also be used in electrospinning. Fibrillar silicate, for example, which exfoliates easier than lamellar silicate such as MMT, has been used in composite nanofibres utilized as reinforcement in dental composites [402]. CdS nanorods, on the other hand, were fabricated into the electrospun fibres from cadmium acetate as a subsequent process step [432].

Mathew *et al.* [329] observed that the addition of the CNTs into electrospun fibres broadened the diameter distribution, and they also reported the roughening of the fibre surface due to CNTs. The dispersion of the particles in solution and in nanofibres is also a key issue in the case of CNT, since poor dispersion of nanotubes may impair properties such as thermal stability of the polymer matrix [423]. Kim *et al.* [50] noticed that MWNTs were well dispersed in the polycarbonate (PC) polymer matrix and well aligned to the fibre direction. Dror *et al.* [478] reported that MWNTs were embedded in the nanofibres as individual elements and they were mostly aligned along the fibre axis. Zhou *et al.* [416] also observed embedding and alignment of MWNTs as well as the stretching of nanotubes during electrospinning. If needed, the dispersion can be enhanced by using dispersing agents and also by functionalization of the surface of CNT [170, 396, 479]. Amide functionalization, for example, enhanced the dispersion stability of MWNTs in formic acid [170], and ester functionalization of SWNTs was advantageous in PU composite prepared from dimethylformamide solution [396].

The tensile strength of the composite fibres has been studied, for example, by Kim *et al.* [50]. They observed necking and slippage of the nanotubes when a tensile stress was applied to the fibre. Sen *et al.* [396] have reported a significant increase of 46 % in the tensile strength of PU nanofibres when incorporating SWNT into a polymer matrix. The mechanical properties depended on the type of SWNT, and chemical functionalization of SWNTs gave rise to even higher tensile strength [396]. CNTs are also used as an additive when preparing precursor nanofibres for carbonization [349, 423, 454-456, 480]. CNTs do not shrink and thus composite fibres containing CNTs are more stable in the pyrolyzation process than neat polymeric fibres [455, 480]. CNTs may promote polymer degradation in the first decomposition step, but at higher temperatures they have a reinforcing effect [423]. Seoul *et al.* [169], on the other hand, report that semiconducting electrospun fibres can be produced with a low CNT loading. The percolation threshold of SWNT was 0.008 wt% in spinning solution or 0.04 wt% in fibre mat [169].

3.2.3 Composites with Spherical Nanoparticles

Lamellar and tubular nanoparticles are often used as reinforcement, but even though this is not the main character of spherical nanoparticles, applications can be found. Spherical particulates can be used to improve wear resistance and hardness of the polymer. Carbon black loading in butyl rubber nanofibres, for example, affected the tensile properties [434]. Spherical nanoparticles are still mainly used because of their functionality, and since the variety of nanoparticles is very extensive a wide variety of properties can also be obtained using them as filler. Two distinguishable application fields of these electrospun nanoparticle composite fibres are their use as catalytic materials for different purposes, and preparation of different kinds of ceramic fibres from metal-containing precursor fibres by the oxidative removal process of the carrier polymer.

Yang *et al.* [149] have described a method for the production of fibre structures containing catalytic material as particles. They suggest that many metals, including platinum, gold, silver, iron, copper, and titanium, may function as catalysts in certain applications. Jo *et al.* [150] described a method for the production of electrospun precursor fibres containing a metallic catalyst for graphitization. The catalyst compound can be, for example, nano-sized transition metals (e.g. Pt, Cu, Fe, Ni, Co), non-transition metals (e.g. Mg, B, Al), compounds such as metal chlorides (e.g. FeCl_2) and metal nitrogen oxides (e.g. $(\text{NH}_3)_4\text{Pt}(\text{NO}_3)_2$), and organic metallic compounds (e.g. nickelcyclooctadiene) [150]. Electrospinning of various kinds of spherical particles has been reported in the literature. Metallic nanoparticles which have been successfully introduced into electrospun fibres include silver [482], which may provide antibacterial property, and gold [483]. However, more frequently the metallic compound is introduced into the solution and metallic nanoparticles have been obtained in electrospun fibres as a result of a subsequent reduction process. This approach has been adopted, for example, with cobalt [449, 484], copper [449, 484], iron [150, 216, 449, 484], nickel [150, 449, 484], palladium [149, 449, 484], platinum [150, 449, 484], and silver [69, 421, 429, 435]. Metal oxides are also more commonly used than neat metallic particles. Titania (TiO_2) is widely used nanoparticle in electrospinning [55, 144, 152, 266, 464]. Nanofibres containing TiO_2 can be used, for example, in photo catalytic reactor elements [152], chemical sensors [113] and photovoltaics such as solar cells [144]. MgO nanoparticle catalyst incorporated into electrospun fibres can be used for protection against chemical warfare agents [100].

Ceramic fibres, obtained from precursor fibres after the oxidative removal of a carrier polymer, are suitable for several applications. Nanofibre mat consisting purely of TiO_2 can be prepared by the electrospinning of titanium tetraisopropoxide [146, 153, 431, 485], titanium lactate [154] or tetrabutyl titanate [99, 486] with a small amount of carrier polymer such as PVP [99, 146, 153, 431, 486], PVA [154] or polyvinyl acetate [485]. Formed nanofibres were subsequently converted into fibrous mat consisting purely of TiO_2 via calcination. Li and Xia have [431] proposed that a similar method can also be used with other oxides such as SnO_2 , SiO_2 , Al_2O_3 and ZrO_2 . TiO_2 nanofibres have also been prepared from isopropoxide precursor without a polymeric additive via electrospinning technique in combination with the sol-gel process [487]. Silica (SiO_2) nanofibres can be used, for example, in hot gas filtration [102] and as a porous absorption membrane [103]. Alumina (Al_2O_3) nanofibres are also suitable for high temperature applications and also for adsorption/chemisorption

of heavy toxic metal [488]. Nanostructured $\text{TiO}_2\text{-SiO}_2$ materials, which have optical properties, high thermal stability, and chemical durability, are suitable for applications such as antireflective coatings and optical chemical sensors [112]. Zinc oxide (ZnO) nanofibres have gas sensing characteristics [114] and photoluminescence properties [173, 489], and nickel ferrite (NiFe_2O_4) nanofibres have magnetic properties [490]. Erbium (Er_2O_3)/ TiO_2 composite and pure TiO_2 fibres can be used in thermo-photovoltaics [146, 153] and pure TiO_2 and TiO_2/CNT composite fibres as a photo catalyst [99, 153-154].

In addition to metals and metal oxides, electrospinning of a wide range of other particles has also been reported. Carbon black, for example, can be used to improve the mechanical behaviour, electrical conductivity, and thermal resistance of the material [434, 491]. Introduction of semi-conducting Ag_2S nanoparticles in PVP fibres made them suitable for use in photo- and thermoelectric materials [145]. Magnetite has been used to gain super paramagnetic properties in fibres [492]. Calcium carbonate (CaCO_3) and hydroxyapatite (HA) calcium phosphate have been included into PCL fibres for use as bone-scaffolding materials to improve cell growth and differentiation [128].

Inclusion of nanoparticles may increase the conductivity of the solution and thus decrease the fibre diameters [100] depending on the nature of the filler, but also increases in fibre diameters have been observed [100, 128]. Non-conducting nanoparticles may increase the viscosity thus leading to increased diameters [128]. The surface structure of nanofibres containing a high amount of nanoparticles is often rough [55, 100, 128] and bead-like irregularities in the diameter composing of agglomerates can occur along the fibre [100].

Uniform dispersion is more easily obtained with spherical nanoparticles than with tubular or lamellar particles. Kim *et al.* [50] demonstrated the preparation of composite fibre using SiO_2 particles, and they observed uniform dispersion of particles in polymer matrix. Kedem *et al.* [152] have demonstrated that it is possible to obtain homogenous nanofibres consisting of both spherical (TiO_2) and tubular (CNT) nanoparticles. Drew *et al.* [266] prepared electrospun TiO_2/PEO nanofibres containing only 25 wt% of polymer, which suggests that the addition of filler particles also enables electrospinning at lower polymer concentrations than is normally possible. We have reported the preparation of nanofibres having an even lower weight fraction of polymer, 9.8 wt% - 15.4 wt%, in TiO_2/PEO fibres [55].

4 Material for Filtration Application

One of the main application areas of electrospun fibres is filtration [8, 18, 22, 32, 53, 68]. This is evident, for example, from the number of nanofibre patents concerning filtration filed by (or assigned to) Donaldson Company [24-28] and others [66, 89-93, 96]. Ngiam *et al.* [493] have noticed that 75 % of the issued nanofibre patents (until 2007) concerned either fabrication or the use of nanofibres in filtration systems. That is not surprising since the existing high efficiency air filters have certain weaknesses. According to Barhate and Ramakrishna [22] current high efficiency filters are viable for particles having diameters of 0.3 μm and above, but their function is insufficient with smaller particles and, for example, pathogenic agents such as viruses. The increased use of deleterious nanoparticles adds more exigencies to the filters.

Electrospinning produces a web consisting of sub-micron fibres as a one-step process. Large webs can be prepared, for example, using multiple nozzles. Polymeric nanofibre webs have several properties such as low basis weight, high permeability and small pore size, which are advantageous in filtration applications [22]. The use of nanofibres offers improved properties compared to conventional filters in laboratory tests and also in actual use [32-33]; the contaminant holding capacity of filter media was improved and the filter life was extended when the predetermined pressure drop was later obtained. Electrospun nanofibre webs are proven to be effective in stopping aerosol particles by both theoretical calculations and experimental measurements [63]. Also simulation of unsteady-state filtration has endorsed the efficiency of nanofibre filtration media [97].

This chapter reviews the scaling-up of electrospinning utilizing a multi-nozzle design for preparation of nanofibre web in Chapter 4.1, and the use of electrospun nanofibres in a filtration application in Chapter 4.2.

4.1 Preparation of Nanofibre Web with Multi-Nozzle Electrospinning

The size of an electrospun web from a single nozzle is relatively large compared to the nozzle size due to the vigorous whipping of the jet, though the coverage of one jet is still limited. The one-nozzle design is useful in small scale laboratory trials, but in the production of fibrous webs different approaches need to be adopted. The production rate of a single electrospinning nozzle is low, typically 0.3 g/nozzle/hour [2], even though the formation speed of fibre can be as high as 100 m/s [317]. Larger coverage and higher productivity can be achieved, for example, using the nozzleless designs presented in Chapter 2.4, but also scaling-up by increasing the amount of nozzles. Both designs have their advantages and disadvantages. The nozzle-design is more controlled since nozzles of fixed sizes are arranged into defined lattice. The multi-nozzle arrangement might, however, be inconvenient compared to nozzleless designs due to its complexity and the blocking tendency of the nozzles [218]. One advantage of the nozzleless design is that jets can spontaneously emerge as close to each other as possible and therefore a higher amount of jets can be obtained from a small area [35, 218, 343]. The shortest possible distance between jets depends on the polymer-solvent system and probably also on process parameters. A nozzle array can rarely have as dense a placement of nozzles as the free solution surface can have jets. That is evidently a slight shortcoming of nozzle arrays. When spinning occurs from the free polymer surface or droplets of uncontrolled sizes, the

fibre diameter distribution can, on the other hand, be large [218]; a fact that favours the use of nozzles. Challenging issues in the electrospinning of nanofibre webs according to Barhate *et al.* [52] are homogeneity of fibre size, evenness of deposition, orientation of fibres and durability of fibre layer. Another issue to be resolved in the scaling-up is productivity.

Nozzles are typically fixed and arranged into some kind of pattern, and the substrate is transferred past the nozzle field. Careful design of multi-nozzles designs is also needed to ensure identical field strength at the tip of each nozzle [10, 391]. Space charge, caused by electrical discharges from the multiple nozzles [287], may hinder the electrospinning process especially if the nozzles are close to each other. Polymer jets from adjacent nozzles are charged with the same polarity and there can be repulsive forces. Theron *et al.* [393] have demonstrated the repulsion between jets by experiments and modelling. They noticed that the smaller internozzle distances led to greater repulsion, and also resulted in an increased deposition rate over a small area because the envelope cones were squeezed from the sides [393]. Tsai and Scheuder-Gibson [57] have made similar observations. They experimented with PA, a three-nozzle design and a rotating collector, and achieved three distinct collection stripes due to the mutual repulsion of the jets. When ionizer was applied between the nozzles and the collector, the charges of the forming fibres were neutralized to some extent, and the three stripes became more diffused and less distinct [57]. We have observed that PVA jets from adjacent nozzles formed merged deposition [288], while PA and PEO were repulsive and produced separate patterns. Due to the repulsion forces the proper arrangement, referring here to the closeness and the array of the nozzles, is important for achieving even coating. The minimum internozzle distance depends on the polymer-solvent system, strength of the electric field, and the diameter of nozzle [494]. Closeness of nozzles can also delay the onset of whipping instability. This has a significant role in the reduction of the fibre diameters, but it may be compensated by increasing the distance to collector thus also increasing the deposition area [393]. An internozzle distance of 8 mm has been found to lead to reasonable stability in multi-jet electrospinning of PVP and PVP/PPy composites [433], and a distance of less than 25 mm disturbed process with PVA [288].

Multi-nozzle designs have been introduced in several patents [194-201, 344, 350-351, 353, 494-498]. The nozzles can be configured in several ways, for example, in the shape a circle or arc, or into different kinds of matrix [496]. One way is to arrange nozzles into straight spinning nozzle packs in the form of row [497], and use multiple rows in sequence. Andrary *et al.* [494] have reported that a certain minimum internozzle distance must be applied not just to avoid electrical interference, but also to prevent a reduced removal rate of the solvent. Bowman *et al.* [499] have studied a multi-nozzle design and noticed inconsistent nanofibre deposition indicating distortions in electric field. They concluded that modifications could be made either to the nozzle or to the chamber designs to ensure even deposition. These modifications might include, for example, the use of air flow or focusing plates [499]. Kim *et al.* [284] studied a five-nozzle array and they used an auxiliary electrode to reduce the distortions. The auxiliary electrode stabilized the spinning process, which led to a reduced deposition area and slightly thicker fibres. Fang *et al.* [391-392] have also used secondary electrodes to shield the nozzles in order to reduce the interference between electrodes. They noticed that the presence of secondary electrodes weakened the strength of the electric field at the nozzle

tip, unless their shape, location and electrical potential were optimized [391]. Chun and Park [497] used control units with same polarity as charged jets for guiding the polymer jets towards the collector.

Solution can dry onto the tip of the nozzle interrupting the process or even making it impossible [137, 159, 241-242, 259-260, 323]. The blocking of the nozzle has been associated with high concentration and viscosity of polymer solution [5, 240, 242], and volatility of the solvent [159, 241-242, 259, 323]. This problem may be overcome, for example, by increasing the boiling point of the solution with co-solvent, running the process at lower temperatures or confining the tip of the nozzle to a solvent saturated atmosphere [323]. Larsen *et al.* [323] have presented a method that should obviate the need of periodic cleaning of the nozzle. They propose the use of a coaxial gas jacket around nozzle. Flow of the inert gas with saturated solvent does not only prevent blocking of the nozzle, but it also suppresses corona discharges and can be used to control the morphology of nanostructures [323]. A similar method with liquid flow of solvent was used by Lallave *et al.* [241]. The method presented by Chu *et al.* [350] combines electrostatic forces and gaseous blowing in the electrospinning process. The properties of gaseous flow can be used for modification of fibrous product while also increasing the production rate. The electrospinning design described by Andrary *et al.* [494] is placed in a chamber, in which temperature, pressure and composition of the atmosphere can all be controlled. The gaseous environment can improve the quality of the electrospun fibres in terms of smaller diameter and smaller diameter distribution of fibres. It can also reduce the corona discharge around the nozzle, permitting operation at higher voltages and thus enhancing electrostatic forces. If the drying rate of the fibres is retarded by adjusting the partial pressure of the liquid vapour in chamber, the stretching can be enhanced [494]. Retarding of the drying rate may also enhance the adhesion, since wet fibres adhere better to the substrate than dry fibres.

4.2 Electrospun Fibres in Filtration Applications

Filter material should have high filtration efficiency: that is the ability to separate the aerosol particles from air flow. The filtration efficiency should remain at a constant level throughout the lifetime of the filter. Filter material should also have low resistance to air flow; in other words, it should have low pressure drop. Good filter material also has a high loading capacity without any significant increase in pressure drop, which is most easily achieved with small packing density and, thus, high porosity. [187] Filters can be divided into coarse and fine filters¹¹. Coarse filters (prefilters), remove the largest particles, which could foul the fine filter layer, from the air stream. HEPA and ULPA filters are used in high efficiency filtration. The filtration efficiency is determined by comparing the particle concentrations upstream, C_1 , and downstream, C_2 , of the filter layer according to (Eq.1)

$$\text{Filtration efficiency} = 100\% * \left(1 - \frac{C_2}{C_1}\right) \quad (1)$$

¹¹ According to EN 779 “*Particulate air filters for general ventilation. Determination of the filtration performance*” the final pressure drop of coarse and fine filters are 250 Pa and 450 Pa, respectively. The arrestance of synthetic dust of coarse filter ranges from < 65 % to ≥ 90 % (classes G1-G4), and the filtration efficiency of 0.4 µm particles of fine filters ranges from < 60 % to ≥ 95 % (classes F5-F9).

Aerosol particles can be deposited on a fibre in filter media by means of five basic mechanisms, which are interception, inertial impaction, diffusion, gravitational settling, and electrostatic attraction [187]. The filtration efficiency of a single fibre is not just a sum, but an interaction effect of all five mechanisms [73], and the dominating mechanism depends, for example, on particle size [22]. The approximated particle ranges of these mechanisms are presented in Figure 8a. Diffusion is the dominant mechanism of the smallest particle sizes having diameters less than $0.3\ \mu\text{m}$ [22, 187], and electrostatic attraction occurs only when aerosol particles and/or fibres hold an electric charge [187]. Performance of a fibrous filter is mainly dependent on particle size, air flow velocity, fibre size and packing density of the filter media [187]. The effects of particle and fibre sizes on filtration efficiency are illustrated in Figure 8b, and the effects of particle size and velocity in Figure 8c. The particle size as well as the air flow velocity varies according to the application. The fibre size and the packing density, on the other hand, depend on the electrospinning design and variables. The fibre diameters of the electrospun fibres can be altered by varying the solution and process parameters, and these parameters also affect the packing density of the electrospun web.

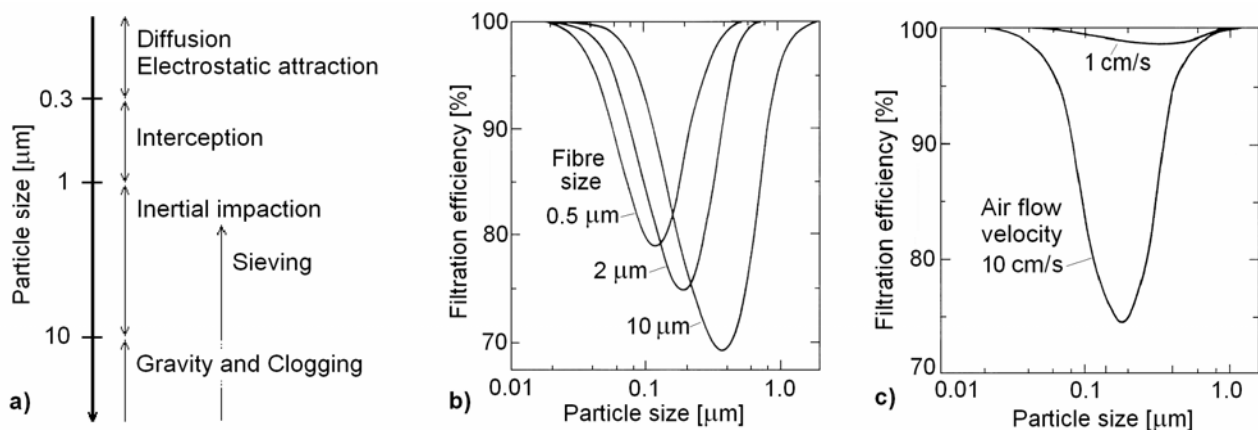


Figure 8. a) Operative particle size in interaction mechanisms [22]; b) The effect of fibre and particle size on filtration efficiency (air flow velocity 10 cm/s, porosity 95 %) [187]; c) The effect of air flow velocity and particle size on filtration efficiency (fibre diameter 2 μm , porosity 95 %) [187].

The nano-scale fibre diameter and the high specific area of the electrospun material are favourable for filtration applications because the filtering efficiency of small particles increases with the decreasing fibre diameter. Higher efficiency is obtained by adjusting the scale of the filter structures to the fineness of the aerosol particles to be filtered [17]. Atmospheric aerosol contains particles of different sizes ranging from the ultrafine range (diameter less than 100 nm) to the coarse range (above 2.5 μm) [187]. The size of viruses, for example, ranges from 10 nm to around 200 nm, bacteria from hundreds of nm's to tens of μm 's, and pollens from tens to hundreds of μm 's. The range of fine particles (less than 2.5 μm) can be divided into nuclei mode (less than 40 nm) and accumulation mode (above 40 nm). Fume and smog particles have diameters in these ranges [187]. Unpurified air, for example, in an industrial workplace may also contain particles on a millimetre scale.

Microfibre filters have a local minimum in filtration efficiency of aerosol particles with a size range of 100 nm - 500 nm [500], which can be seen in Figure 8b. This size is called the most penetrating particle size (MPPS) and especially in this size range the application of electrospun nanofibres can make a major impact [500].

Zhou *et al.* [87] studied the filtration efficiency of melt-electrospun PLA fibres. They compared the effect of sub-micron PLA fibre layer and 10 μm PLA fibre layer on filtering efficiency and pressure drop of a standard filter media. Filtering efficiency was enhanced regardless of fibre size. Sub-micron sized fibres were more efficient in the fine particle range, and microfibres were better when particle size was around 1 μm or above [87]. Electrospun nanofibres can have as small a diameter as a few nanometres, but typical diameters range from some tens to some hundreds of nanometres. Chung *et al.* [27] have suggested that the fibre size in the electrospun filtration layer should preferably be between 50 nm and 500 nm in order to keep filtration efficiency and strength in balance. Schreuder-Gibson and Gibson [60] observed that only 0.5 g/m^2 PA6 nanofibre layer, having fibre diameters around 100 nm, filtered 99.9 % of aerosol particles having diameters of 1 μm - 5 μm from the air flow of 1 m/min. Yun *et al.* [68] compared nanoparticle (<0.08 μm) penetration of electrospun filter with commercial HEPA filters. They found that smaller fibre mass was required but higher pressure drop was obtained with electrospun material [68]. Filtration efficiency increases with the increasing amount of nanofibres as does the pressure drop, and thus the thickness of the electrospun nanofibre layer must be adjusted to an optimum level.

Small fibre diameter increases the specific surface area; for nanofibres having diameters from 500 nm to 5 nm the surface area per unit mass ranges from 10 m^2/g to 1000 m^2/g [9], see Figure 9. The specific area of the web can, however, also be increased without decreasing the fibre diameter. Doiphode *et al.* [219] polymerized cyanoacrylate monomer on the surfaces of electrospun fibres and obtained fibrous polycyanoacrylate structures. Hou and Reneker [216, 449] used the surface of iron-containing carbonized nanofibre as a substrate for the preparation of MWNTs using the CVD method. Growing MWNTs formed a unique hierarchical structure on the fibre surfaces [216]. Electrospinning of polymer blends or self-organising co-polymers can produce fibres with a micro phase-separated structure and by selective removal of other components can lead to a nanoporous structure [Paper I, 409, 419, 458-459].

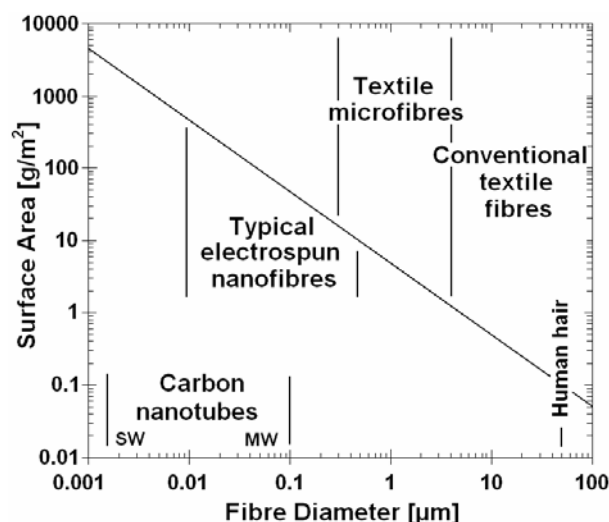


Figure 9. Effect of fibre diameter on surface area of fibrous web. [9]

Other properties of electrospun webs that are advantageous to filtration applications are high porosity, good interconnectivity of pores, and the possibility to add functionality into electrospun fibres [22, 52]. According to

Greiner and Wendorff [17] the porosity, the average pore size, and the specific surface area are the three most important parameters determining the diffusion of gas, air flow resistance and filtration efficiency of nonwoven materials. In an electrospun membrane high porosity is combined with small pore size [63] and typically a tortuous, interconnected pore structure. Distances between electrospun nanofibres typically range from 10 nm to 25 μm [27], and the porosity of the electrospun nanofibre layer can be higher than 80 % [501]. In an electrospun structure the amount of blind pores is negligible, but the existence of hourglass-like shaped pores with thinner throats is possible [501]. Besides porosity, the pore throat diameters are also important in applications such as filtration [501]. The porosity and the packing density of the electrospun web can be adjusted by varying solution parameters such as concentration [98] affecting the fibre diameter, and process parameters such as distance [52] affecting the morphology of the web. Short distances may lead to inadequate drying of fibres, which become fused to each other and spread onto the collector to form a densely packed membrane instead of a fibrous web [52].

The gas permeability of fibrous web depends on fibre diameter and porosity [98]. Schreuder-Gibson *et al.* [61] have studied transport properties such as the moisture vapour diffusion resistance of electrospun membranes for use as a protective layer in fabrics for protective clothing. They found that electrospun membranes had exceptional breathability accompanied with wind resistance [61]. Dense packing of small fibres leads to higher filtering efficiency of small particles, but the pressure drop is also increased, and therefore balancing of properties are needed to gain an optimal filter product [73]. The use of electrospun nanofibres makes the balancing easier, since their filtration efficiency increases faster than the pressure drop [32]. Yun *et al.* [68] compared electrospun material with commercial HEPA and ULPA filters of larger fibres. The pressure drop of the electrospun web was the lowest, while the penetration of nanoparticles was the same for all materials [68]. The advantage of nanofibres was also demonstrated by Zhou *et al.* [87] who compared the effect of sub-micron PLA fibre layer and 10 μm PLA fibre layer on the filtration properties of standard filter media. A marked difference between these layers was found in pressure drop. When same amount of these fibres (0.1 g/m^2) was applied in the filter media the increase in the pressure drop of 10 μm fibres was 7.5 %, and of sub-micron fibres only 3 % compared to bare filter media [87]. This is caused by the slip-flow effect [32, 187]. In the case of conventional fibres the air velocity on the surface of the fibre is considered to be zero, but when fibre diameters are less than 0.5 μm , the movements of molecules in the air, having a mean free path of 0.066 μm , are significant compared to the fibre size. Therefore instead of a no-slip condition, the air is slipping at the surfaces of the fibre, which reduces the pressure drop [32, 187]. Slip-flow also transfers more particles to the vicinity of the fibre and thereby enhances filtration efficiency due to higher diffusion, interception and inertial impaction rates [32].

The filtration efficiency and the pressure drop of the electrospun web are advantageous for filtration, but the filter material also has to satisfy other requirements [27]. Textile materials like nonwovens and woven or knitted fabrics can be coated using the electrospinning method to form a barrier layer on protective clothing and masks. In these applications the filtration layer must also meet the demands of permeability, resistance to penetration by specific fluids, flammability, laundering, mechanical durability and strength, and wearer comfort [34]. Respirators, in particular must meet high requirements; they must be efficient without too high a

pressure drop to ensure ease of breathing, but the materials must also be antitoxic and resistant to filtered particles and water [74]. In other filtration application, the materials and structures employed should be resistant, for example, to heat, humidity, high flow rates, operational abrasion, sub-micron particulates and reactive particulates. They should also permit the cleaning of filters, reverse pulse cleaning and meet other conditions according to the application and operating conditions of filters [27]. These properties are dependent on many factors such as chemical composition and molecular weight of the used polymer, the structure of the web, and properties of the substrate material.

Several materials can be used in the preparation of electrospun filter layers, and, thus, properties of a material can be adjusted to the specific needs of the intended application. Frequently mentioned polymers in articles on the use of electrospun fibres in filtration applications are PA [27, 30, 34, 54, 57, 59-60, 63-67], PAN [24, 51-52, 57, 62, 64, 68-70], PU [34, 56-57, 59, 61, 63, 71-72] and PVA [67, 73-77]. In addition to these, for example, PS [57, 62, 78-79], cellulose and derivatives [69, 80-81, 84], PEO [56-57, 67], PC [56-57, 59, 86], polysulfones [72, 82-83], polybenzimidazole (PBI) [59, 63], fluoropolymers [84-85], polyvinylidene chloride [24], PCL [57], PVC [69], PLA [87], and polyimide [88] have also been mentioned in the literature.

The thickness of the electrospun nanofibre web can be on a sub-micron scale [27]. The mechanical strength of such a thin web is typically limited and it is easily punctured or torn apart. Filtered particles can also reduce durability, mechanically grating against the nanofibres [34]. Therefore electrospun nanofibres are typically used as effective filtering layers on fibrous, supporting substrates [30, 34]. The substrate material can also operate as a coarse filter [34, 85]. The electrospun fibre layer and its ability to prevent particulates determine the filtering efficiency of the composite structure, while the structural properties of the filter media such as stiffness, strength and pleatability are provided by the substrate [27]. The use of substrates being or resembling conventional filter materials allows the use of normal filter media pleating and element handling equipment [32]. The amount of layers may vary as well as their material [24, 27, 62]. Face-to-face lamination of two nanofibre-coated substrates may provide enhanced durability of the composite [34]. A sandwich structure can also be made of electrospun layers with different fibre diameters in such a way that smaller fibres are covered from both sides with layer of thicker and thus stronger electrospun fibres [84].

The nanofibre layer has to be adaptable to the movements of the substrate without breaking or delaminating. The durability of nanofibres depends according to Graham *et al.* [34], for example, on the quantity of nanofibres and the weight and rigidity of the substrate material. When composite material consisting of a fibrous substrate and a nanofibre layer is stretched, bent or scrubbed, the coating layer, which has numerous binding sites to many fibres of substrate, can easily be destroyed by the gross movement of the substrate fibres, especially if the strain capacity of the nanofibres is also limited. When the fibres of the substrate material are rigid forming a tightly bonded structure, their movement with respect to each other is limited compared to more loose structures. Therefore, for example, flat spun bonded nonwoven material is, in principle, a better substrate than woven fabric, which can have fibre ends sticking out of its surface. The heavy weight of substrate instead of light weight and also thin nanofibre layers instead of thick ones are

preferable in terms of durability [34]. Gibson *et al.* [63] have studied many properties of the electrospun nanofibre layers with respect to their use in protective clothing. They have managed to produce electrospun structures with a strain capacity of more than 200 % using elastomeric membrane materials [63]. Highly elastic electrospun fibres with elongation capacity of over 1300 % have also been produced from highly branched segmented polyurethane ureas [250].

Chung *et al.* [27] have discussed adhesion between the nanofibre layer and the substrate in order to prevent the delamination of the effective nanofibre layer due to the reverse pulse cleaning technique and other mechanical stresses. Good adhesion may be achieved by solvent effects in fibre formation or by post treatment with heat or pressure even though polymer characteristics such as chemical interaction also play an important role. One possible method to improve adhesion is also the use of polymer plasticizer with solvent or steam treatment [27]. Shutov [85] pointed out that if electrospun fibres contain a small amount of residual solvent, the evaporation of such a residue can glue the joints between fibres, and thus improve the mechanical strength of the fibre layer. This approach does not affect the fibrous form of electrospun fibres or the porous structure of the material, which are important in filtration [85]. Shutov and Astakhov [84] have used a layer of damp, thicker fibres deposited onto the substrate to form an adhesive layer onto which smaller fibres have been applied. This way a sandwich material with good filtering and mechanical properties is obtained [84]. Good adhesion was also observed when using the same polymer as substrate and in nanofibres, for example, electrospun cellulose nanofibres on cellulose filter media [80].

Improved functionality can be achieved in the electrospun filtration layer using additives or functionalizing the electrospun fibres by other means. Huang *et al.* [88] included rod-like polyimide macromolecules in the spinning solution and obtained electrospun nanofibres with excellent mechanical properties and heat resistance. TiO₂ incorporated into electrospun filter media can act as photo catalyst [55, 99, 152, 485] in degradation of impurities captured by the filter. For example, composite nanofibre mat of TiO₂/MWNTs obtained by calcination of carrier polymer after electrospinning has promising applications in water purification [99]. A specific catalyst for chemical warfare agents has also been incorporated into electrospun structures [34, 100], and incorporation of the catalyst into nanofibres may lead to an enhanced depletion rate of the stimulant compared to using catalyst alone [34]. Chronakis *et al.* [101] suggest that selective molecular recognition sites introduced into the electrospun filter fibres can provide higher efficiency in compound separation. These recognition sites can select molecules according to their shape and to the position of their functional groups [101]. Functionalization of fibre surface with specific selective agents is also used in affinity membranes for water treatment [14]. Permanent antimicrobial activity can be obtained in electrospun filter media. Silver nitrate has been added to polymer solution prior to electrospinning and subsequent photo reduction process has been used to obtain silver nanoparticles into electrospun fibres [69, 421, 429, 435], but also metallic silver particles can be used [482]. Antimicrobial activity has also been achieved using quaternary ammonium [86] or chlorinated N-halamine compounds [403]. The use of salt compound can also improve the electrospinnability of the solution [86] due to improved conductivity. Quaternary ammonium groups leading to antimicrobial activity can also be synthesized into polymer chain and thus included in the electrospun nanofibre filter [71].

Electret filters can be prepared with several methods including corona charging and tribocharging of the filter media, but the electrospinning method can combine the preparation and charging of the fibrous web into a one-step process [56]. Electrical charges, possibly remaining in the electrospun web, may enhance the filtration efficiency due to electrostatic attraction. Electrospun fibres, prepared in the electric field, may either dissipate or retain charges depending on the electrical properties of the polymer [7]. Tsai and Schreuder-Gibson [57-58] were interested in web formation for filtration applications of various polymers. They noticed that polar materials such as PA, PU, PEO and PCL did not retain the residual charges while non-polar polymers, such as PS, PC and PAN did [57]. Schreuder-Gibson *et al.* [62] studied and compared the charge retention and the filtration properties of different types of electrospun web constructions. They noticed that some single-, multi-layered and bi-component webs retained a surface charge over a 20-hour period in thousands of volts - around the same level as 10 minutes after electrospinning. This charge was bled off during three month storage and only three out of eight samples retained their charges up to hundreds of volts after that period [62]. Only weak dependence of filtration efficiency on the surface charge was found [62], and also Yun *et al.* [68] have stated that the effect of electrostatic attraction in the operation of the electrospun filters was negligible.

Besides traditional aerosol filtration, electrospun nanofibres can be used for special air filters and filtration of liquids. Tovmash *et al.* [77] prepared a highly effective vapour sorption filter by carbonization of electrospun PVA membrane. Sorption capacity of initial electrospun PVA membrane can increase 2-fold by thermo-oxidation process and 20-fold by carbonization process, exceeding the sorption capacity of commercial reference materials 2 to 3-fold [77]. The use of ceramic materials in nanofibres, on the other hand, enables the application of such material in hot gas filtration [102]. Ultra- and nanofilters for water treatment are conventionally porous membranes prepared by the phase immersion method, but the flux rate of these membranes is relatively low [51]. A new type of high flux rate filter containing electrospun fibres has a layered structure; the electrospun layer is combined with a hydrophilic water-permeable but non-porous coating layer, and possibly with conventional microfibrinous nonwoven as a support layer. The composition of the effective layers can be, for example, PAN [51] or PVA nanofibre layer [75-76] with chitosan coating [51], PVA [76] or some other hydro gel coating [75]. The coalescing filters are used to separate small liquid droplets from another liquid phase or from gas streams, their typical application being water-in-oil dispersions. Electrospun polymeric nanofibres have been mixed with micro glass fibres to form a coalescence filter with improved efficiency [64-65, 78]. Affinity membranes contain specific capturing agents, ligands on their surface so that they can remove specific target molecules such as organic compounds and heavy metals from waste water [14]. Affinity membrane structures based on electrospun web have been demonstrated, for example, using regenerated cellulose [81] and polysulphones [82-83], and the ligands used for the organic compound were bovine serum albumin [82] and Cibacron Blue F3GA dye molecule [81, 83]. Ceramic nanomaterials, for example, hydrated alumina/alumina hydroxide and iron oxides, can be used for functionalization of polymeric nanofibre membranes for applications such as heavy metal removal from waste water [14]. Electrospun nanofibre membrane has also been found feasible for use in artificial renal chips for filtration of blood cells from the blood stream in dialysis [72].

5 Experimental

The experimental part of this thesis consists of many separate studies, which are reported in Papers I - VI. In these studies nanofibres were prepared using different kinds of polymer and composite solutions. Electrospinning trials were carried out using single-nozzle eSp2 equipment and eSp3 equipment with multiple nozzles. Methods of analysis depended on the objectives of each study. This chapter reviews the materials in Chapter 5.1, the electrospinning set-ups in Chapter 5.2, and the main methods of analysis used in these studies in Chapter 5.3.

5.1 Materials

A study reported in Paper I was carried out using self-organizing block-co-polymer. The studies reported in Papers II - VI were carried out using different grades of polyvinyl alcohols and polyamides. They include laboratory grade polymers, commercial industrial grade polymers, and polymer synthesized specifically for these trials. In Paper II lamellar filler was introduced into electrospun PVA and PA fibres and, in a study [55] reported outside the papers of this thesis, fibres composed mainly of spherical nano-sized TiO_2 were electrospun using PEO as a carrier polymer. The polymers and nanoparticles used in studies are summarized in Table 2.

Table 2. Polymers and nanoparticles used in experiments.

Paper	Polymer or particle	Source	Details
I	PS- <i>b</i> -P4VP(PDP) _{1.0}	Polymer Source Inc.	Two grades: Mw (PS / P4VP) 238,100 / 49,500 g/mol; and 301,000 / 19,600 g/mol
II	PVA Mowiol 28-99	Kuraray Specialities	Neat PVA , viscosity of 28 ± 2 cP (4 wt% in 20°C)
II	PVA KL-318	Kuraray Specialities	Anionic PVA modified with hydroxyl groups; viscosity 20 - 30 cP (4 wt% in 20°C)
II	PVA R1130	Kuraray Specialities	Nonionic PVA functionalized with silanol groups; viscosity of 20 - 30 cP (4 wt% in 20°C)
II	PVA	HUT	Synthesized using vinyl acetate
II, III & V	PA66	Fluka Chemika	Viscosity 145 cP (10 wt% in RT at TUT)
II	PA66	HUT	Synthesized using 1,6-diaminohexane, dichloromethane and adipoyl chloride
II	MMT Cloisite®Na ⁺	Southern Clay products	Sodium MMT
II	MMT Cloisite®15	Southern Clay products	MMT organomodified with a quaternary ammonium salt
IV	PVA	Merck	M _w 72,000 g/mol; viscosity 145 cP (10 wt% in RT at TUT)
V & IV	PA6 Ultramid B5 Natur	BASF	Mn=85,078; Mw=197,951; PDI=2.327; viscosity 650 cP (10 wt% in RT at TUT)
V	PA612	Cathay Biotechnology Group	Viscosity 85 cP (10 wt% in RT at TUT)
V	PA614	Cathay Biotechnology Group	Not soluble in RT
V	PA1012	Cathay Biotechnology Group	Not soluble in RT
V	PA1014	Cathay Biotechnology Group	Not soluble in RT
VI	PA6 Durethan B 30 S	Bayer	Mn=43,659; Mw=79,689; PDI=1.825
-	TiO ₂	Kemira Pigments	Anatase type
-	PEO	Aldrich	Mw 600,000

The solution preparation method depended on the polymer. Typically polymers were dissolved in heated solvent and stirred in a magnetic stirrer until the polymer was fully dissolved and the solution was clear. *Brookfield DV-II+* viscometer was used to measure the viscosities of the solutions when cooled down to room temperature. The preparation method was also varied in Paper II when nano-sized clay was used as filler. In first method components were mixed in solution utilizing a different feeding order of components. In the second method polymer was *in-situ* polymerized in the presence of clay to form composite and the solution was prepared from premixed composite.

5.2 Electrospinning

Two electrospinning set-ups used in the experiments are presented in Figure 10. Most trials were done with eSp2, a design using individual nozzles and intended for stationary samples (Figure 10a). A study reported in Paper VI was carried out with eSp3 equipment, which consists of multiple nozzles and which was built for preparation of continuous nanofibre coatings (Figure 10b). A horizontal electric field, which prevents staining of the collector and dripping of the polymer solution onto substrate, is used in both set-ups. The bipolar high voltage sources are also identical. *Simco Chagemaster BP 50* is capable of producing both positive and negative voltages up to 50 kV (2 mA) simultaneously from its two outlets. Typically the nozzle(s) was charged positively and the collector was either charged negatively or grounded. *Luer* needles of different sizes and lengths were used in both devices as nozzles.

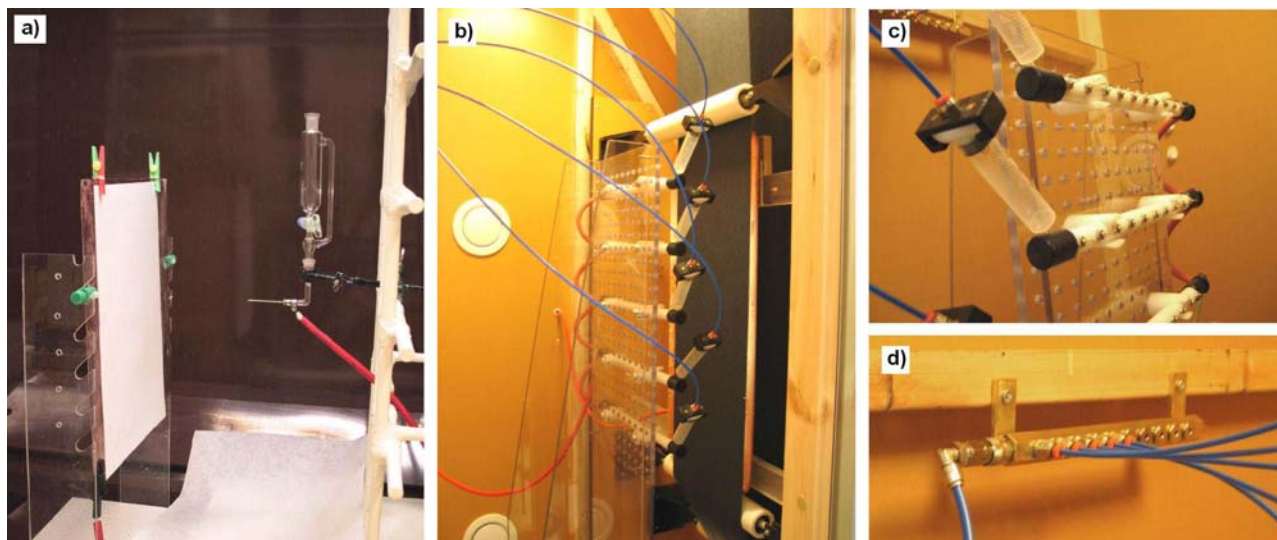


Figure 10. Electrospinning set-ups: a) eSp2 with one nozzle for stationary sample, and b) operational eSp3 with five tubes, which attached to rack. Pressurized feeding has pressure equalization and distribution system (c & d).

The nozzle system of the eSp2 consists of a curved glass pipe having a ground-joint on its upper end for the solution feeding, and a metallic luer lock socket on its lower end for the nozzle and for the voltage source connection. The glass nozzle system(s) is attached to a rack with clamps. A square copper plate (400 mm*400 mm) used as a collector is attached to a separate rack so that the working distance can be adjusted. Besides the plate, a rotating disc collector was also used [Paper I]. The eSp2 equipment is located

in a fume chamber in order to protect the user from the solvent vapours and from the occasional loose nanofibres.

The nozzle system of the eSpin3 consists of tubes with multiple removable nozzles having an internozzle distance of 30 mm. These tubes are made of insulating plastic and are attached to a moving rack. A charging electrode, a metal pin, connected to the voltage source from one end of the tube is located inside the tube and, thus, inside the solution. Solution is fed from the other end of the tube with a syringe, the plunger of which is replaced with a pressurized nitrogen gas juncture to control the feeding (Figure 10c). All tubes are subjected to the same applied voltage and to the same applied pressure (Figure 10d). The nozzle rack and rectangular collector plate are located inside a wooden cabin with a controlled exhaust ventilation system. Electrospun fibres can be prepared continuously onto a moving web. The web winding system is located outside and above the cabin. The web moves down to the electrospinning zone in front of the fixed collector plate sweeping its surface, and moves back up behind the plate.

5.3 *Methods of Analysis*

The imaging of the electrospun fibres can be done using different methods, but characterization of the properties of the individual electrospun fibres is difficult due to their small size. It is not easy to find analysing tools to measure properties of that scale, and also the sampling of individual fibres would be difficult. Since electrospun fibres are typically produced in the form of fibrous mat, a logical step is to analyse and characterize the mat.

The appearance of the fibres was observed with scanning electron microscopy (SEM) in all papers. AFM, transmission electron microscopy (TEM), nuclear magnetic resonance (NMR) spectroscopy, and small angle X-ray scattering (SAXS) were used to analyse the internal structure of the self-assembled electrospun fibres in Paper I. Elemental analysis was used for observation of the distribution of the nanoparticles within nanofibres in Paper II. The appearance on the electrospun coatings was observed visually from samples made on aluminium foil or dark colour substrate in Papers II and IV. Contact angle and water penetration measurements were used to analyse the nanofibre layers containing clay particles in Paper II. Filtering efficiency and pressure drop were measured from the filter samples in Papers III and V. Elongation of the nanofibre layer was studied in Paper III with tensile testing machine. In Paper IV the electrostatic field of the electrospinning design was modelled using the finite element method (FEM). Measurement methods and the devices used with the common methods are described in corresponding papers, but descriptions of two customized methods are included here. The system used in the filtration efficiency and the pressure drop measurements at VTT are described in Chapter 5.3.1, and the modelling of the electric field of the electrospinning with eSp2is described in Chapter 5.3.2.

5.3.1 Filtration Measurements

The pressure drop and the filtration efficiency measurements were made with a test system, the principle of which is shown in Figure 11. A diethylhexylsebacate test aerosol generated with a pneumatic aerosol nebuliser was mixed into the HEPA filtered supply air. The filter material sample to be measured was fixed to

the filter holder, which was positioned inside the test duct. Air flow through the sample was adjusted to a value corresponding to the desired air velocity (10 cm/s). The air flow rate was measured with an ASME mfc small-bore flow meter. The pressure drop across the filter material was measured with a DPM TT 470S micro manometer. The fractional removal efficiency was determined by measuring particle concentrations from upstream and downstream of the filter sample. The particle size distributions were determined with an optical particle size analyzer PMS LAS-X.

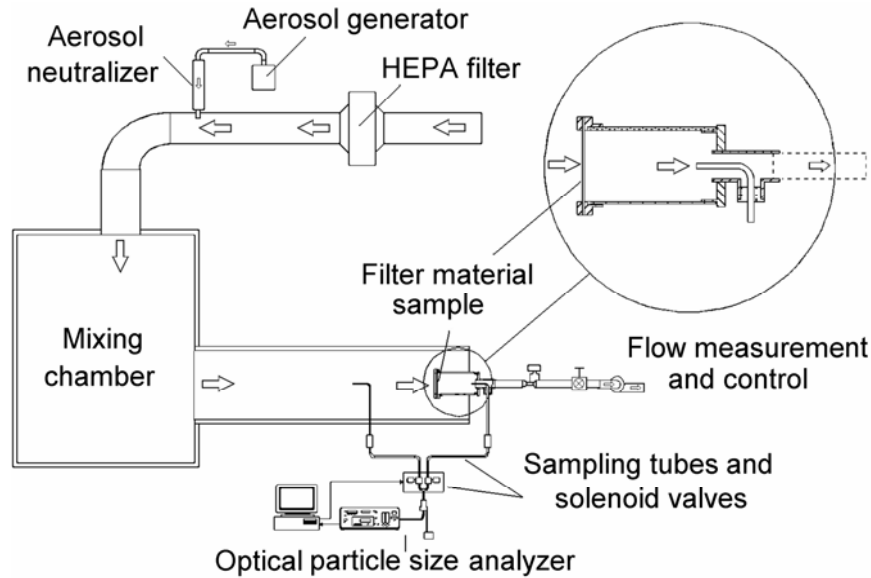


Figure 11. Principle of the filtration efficiency test system.

5.3.2 Modelling

The modelling was made with the Opera 3D (Vector Fields Ltd) software based on the fundamental equations of the electromagnetic theory using the FEM with a tetrahedral mesh. The spinning process was treated as electrostatic, assuming no changes of electric field during time. Charge densities of materials were also assumed to be zero. The mathematical problem solved was a Laplacian kind of partial differential, equation (Eq. 2)

$$\nabla \cdot \epsilon \nabla V = 0 \quad (2)$$

where ϵ is the permittivity of a material and V is the potential. Potential was related to electric field by a negative gradient.

In modelling of the eSp1, (predecessor of eSp2 with similar structure, see Figure 12a), the symmetry was exploited so that only a half of the system was calculated consisting of half the nozzle and half the collector plate (Figure 12b). The stable part of the polymer solution jet was modelled as a cylinder of 50 mm in length and 0.2 mm in diameter, having a permittivity of 80. The substrate having a width of 400 mm was considered to be in contact with the plate.

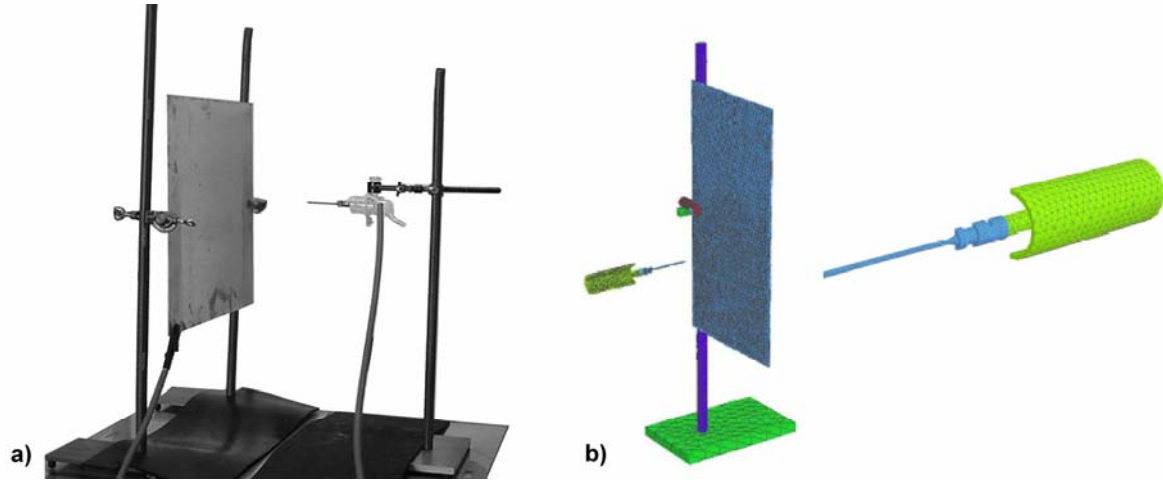


Figure 12. a) Electrode design in single-nozzle model, and b) the half of the system and the half of the nozzle with the finite elements.

The problem symmetry and the symmetry of the field were implied by the potential boundary condition. The Neumann type boundary, $\partial V/\partial n = 0$, was assigned to the symmetry plane and the boundary condition of the Dirichlet type, $V = 0$, was assigned to the exterior surfaces of the calculating volume. The fixed potentials were given to the surfaces connected to the power supply. The floating conductive parts of the system were modelled as materials having very high permittivity. The calculating volume, in which the equation is satisfied, was divided into small volumes, finite elements. Within each finite element a certain polynomial was used to approximate the solution.

The origin of the coordinate system was in the middle of the collector plate. The main observation plane (440 mm x 440 mm) was set between the nozzle and the collector plate according to Figure 13. The plane was 10 mm apart from the collector plate, having a z-coordinate of -10 mm. The parameters of the basic model were a distance of 150 mm and voltage of 40 kV between the nozzle (20 kV) and the collector (-20 kV). This arrangement produced an even fibre coating with 10 wt% solution of PVA and eSp2 equipment. Variations were made to the model by changing the voltage and the distance [Paper IV] as well as the number of the nozzles [288].

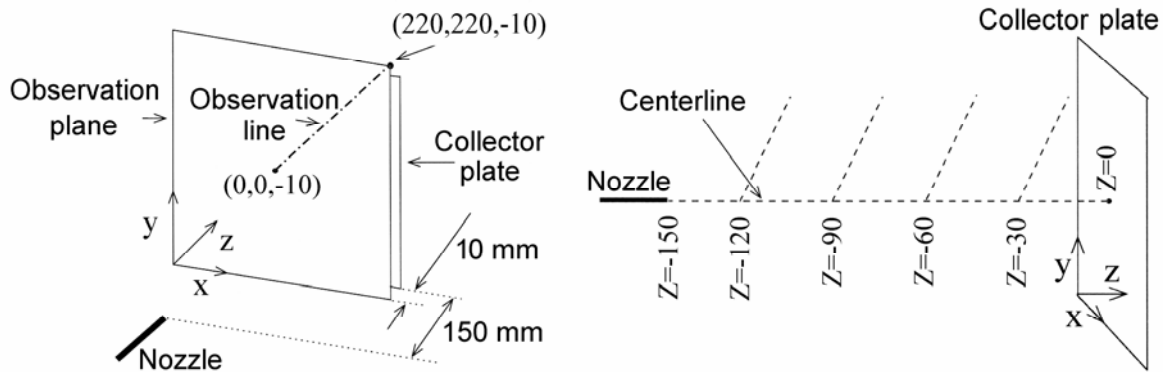


Figure 13. The observation plane of the model is between the collector plate and the nozzle. Its distance from the plate can be changed.

6 Preparation of Nanostructured Fibre Composites

Preparation of fibrous composites was conducted using different materials. In addition to neat polymers we modified the fibres. Initially we considered highly porous fibres for improved static electrical properties and adsorption surface, but subsequently we also decided to use the additives for the functionalization of the fibres. This chapter reviews the preparation of nanofibres from the neat polymers in Chapter 6.1, from the self-organizing co-polymer material in Chapter 6.2, and from the polymer composites containing nanofiller in Chapter 6.3. The effect of various solutions and process parameters on the properties of electrospun fibres is also discussed, mainly in conjunction with the neat polymers.

6.1 Neat Polymers

Polymer jet should remain coherent in electrospinning so that fibres can be formed. Factors affecting the cohesion have been discussed in Chapter 2, but with the neat polymer in a binary system with the solvent, it is mainly dependent on polymer concentration. At low concentrations only beads are formed. An increase in concentration increases the fibre diameters and the quantity of fibre filaments along the beads. A further increase in concentration causes merging of the beads into growing fibres: spherical beads become bigger, their shape becomes more spindle-like and the interbead distance increases as the viscosity increases [214]. This *change in morphology*, which is typical of electrospinning, was observed with the neat polymers used in our experiments. The changes in morphology of PVA (used in Paper IV) and PA66 (used in Papers III and V) are presented in Figure 14.

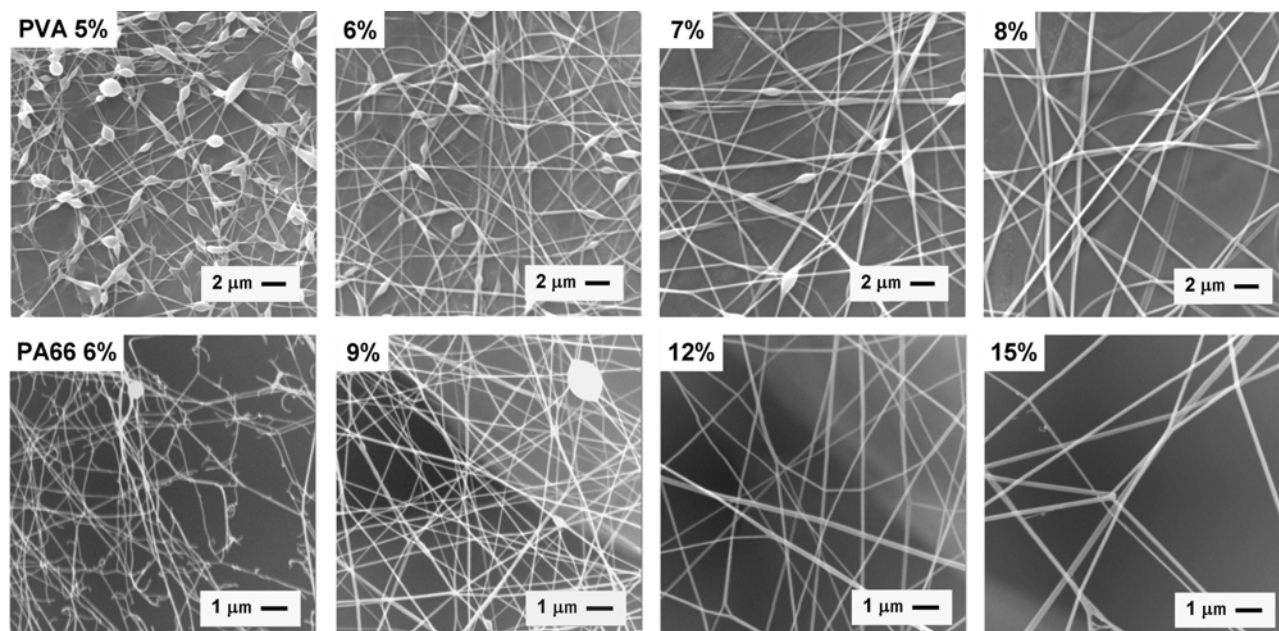


Figure 14. *Change in morphology with increasing concentration from beaded fibres to smooth fibres with larger diameter.*

The effects of process parameters on fibre diameters and the fibre diameter distribution of electrospun PA6 have been studied in Paper VI utilizing orthogonal experimental design. The viscosity of the solution was the main parameter determining the fibre diameters and also the salt content of the solution and the strength of

the electric field had a strong effect on it, see Figure 15. The dependency curves with concave shapes were obtained with the voltage, the distance and the electric field. This was caused by opposing phenomena, which were acting simultaneously. Higher voltage and, thus, higher electric field can cause a higher mass flow [327] leading to thicker fibres [310]. On the other hand, however, the higher voltage induces electrostatic forces on the jet [147] enhancing the whipping, which favours the formation of thinner fibres [310]. A larger distance may also enhance the evaporation of solvent, leading to thinner fibres, regardless of the reduced electric field. In our experiments the salt increased the fibre diameters. Increment of salt increased the conductivity which, as with electric field, may either increase the mass flow leading to thicker fibres, or increase the whipping leading to thinner fibres [262]. In our system the former phenomenon was predominant. In a study reported in Paper IV the fibre diameters of PVA depended on the strength of the electric field. The smallest fibres were obtained with the shortest distance as well as with the highest voltage.

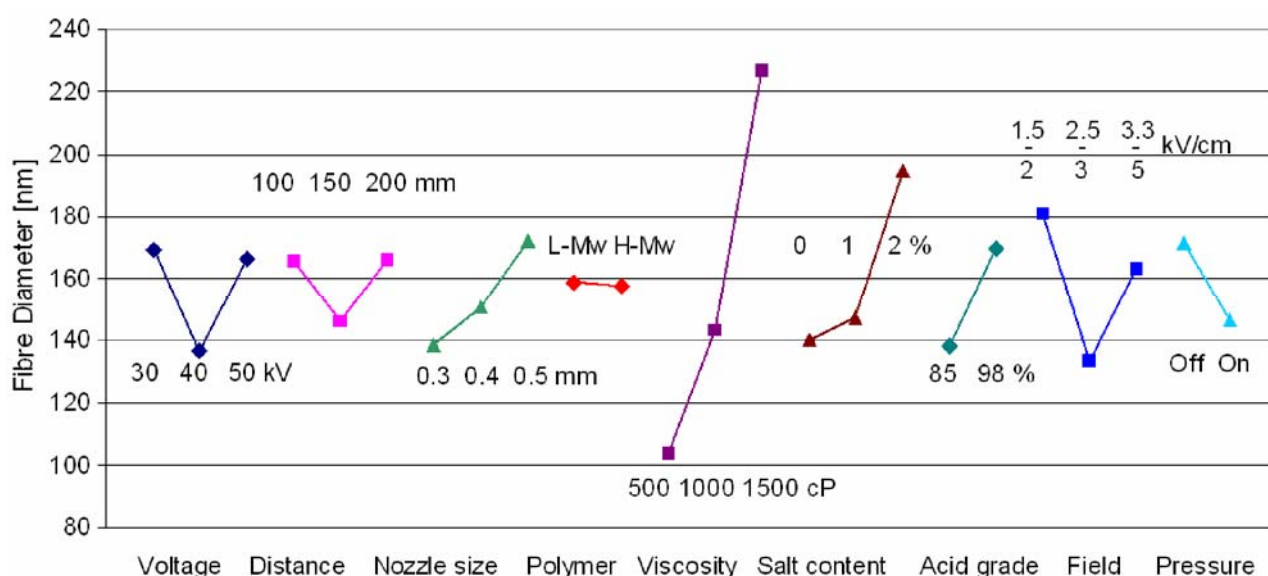


Figure 15. Mean effects of the parameters on the fibre diameter of PA6.

In a study presented in Paper VI the variation of the PA6 fibre size distribution with altering levels of parameters was relatively small. The main parameters affecting the fibre diameter distribution seemed to be distance, nozzle size, and feeding pressure. In a study reported in Paper IV we observed that fibre diameters can also vary slightly in different parts of the deposition pattern even though this variation was not significant.

The electrospinnability of neat polymer solutions can be diminished for several reasons. In the case of polyelectrolytes, for example, the solution conditions such as pH affect the chain conformation of polyelectrolyte in solution [502]. If the chain conformation is, for any reason, suppressed, the amount of chain entanglements is reduced, which affects the fibre formation. The higher polyamides used in a study presented in Paper V had longer diacids and diamines segments than conventional polyamides such as PA6 and PA66. The solubility of the higher polyamides to polar formic acid was reduced with their lengthening non-polar structural segments, which affected electrospinnability. Solutions of PA614, PA1012 and PA1014 had to be electrospun while warm. Heating decreases the value of χ -parameter, which enhances solvation [247]. We also found that heating affected, for example, the fibre diameters. In a parameter study [Paper VI],

on the other hand, the fibre formation of two PA6 solutions was impaired because the conductivity of the solution was too high.

6.2 Self-Organizing Polymers

The block-co-polymer/amphiphile system of polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) and 3-n-pentadecylphenol (PDP) is capable of self-organization in bulk material [Paper I]. Self-assembly between PS and P4VP(PDP) leads to cylindrical assembly, in which P4VP(PDP) domains have lamellar assembly between the non-polar alkyl tails of PDP and the polar P4VP chains. In our study a 13 wt% solution of PS-*b*-P4VP(PDP)_{1.0} grade, having molecular weights of 238,100 g/mol and 49,500 g/mol for PS and P4VP components respectively, was prepared for electrospinning. Even though the viscosity of the solution was quite low, not much higher than that of water, the fibre formation was successful. Some beads with a collapsed raisin-like structure appeared along the fibres (see Figure 16a). The fibres were collected on the sharp edge of a rotating disc collector and therefore they were somewhat oriented.

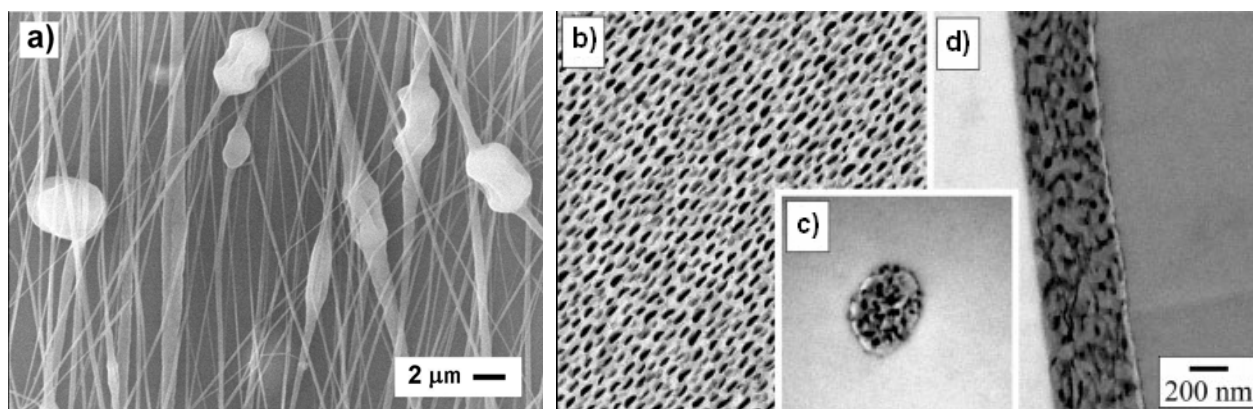


Figure 16. a) The appearance of electrospun PS-*b*-P4VP fibre. TEM images of b) PS matrix of the bulk sample, c) cross-sectional sample of electrospun fibre and d) structure of electrospun fibre along the sample.

TEM imaging revealed that the self-organisation also occurred during electrospinning, but the order of the self-organized structure was relatively poor compared to the bulk sample (see Figure 16b-d). The reason for the reduced order was the rapid fibre formation process of electrospinning. Analyses showed that the length scale of the cylindrical structure caused by self-assembly between PS and P4VP(PDP) was around 30 nm. Within P4VP(PDP) domains the length scale of the lamellar self-assembly was 3.9 nm. Hydrogen bonding of PDP tolerated the harsh electrospinning conditions. When P4VP(PDP) domains were selectively removed using methanol, porous PS fibres were obtained. A similar structure with slightly different dimensions and shapes and slightly improved order was obtained using the other co-polymer grade with different molecular weights (301,000 g/mol and 19,600 g/mol for PS and P4VP, respectively). It was thus shown that the size of the pores and structure of the porous structure can be controlled by the choice of polymers. The self-assembly may offer a feasible tool to form a uniform porous structure throughout the fibre, and such a porous material may have applications as filters and functional fabrics.

6.3 Fillers in Electrospun Fibres

Nanofillers can be used to enhance properties or obtain functionalities in electrospun fibres [13, 50]. Interaction between the filler and polymer has great importance for the behaviour of the composite in the solution, the morphology of the forming fibre and the surface properties of the fibre. The challenge of using any kind of nanoparticle filler is to obtain good dispersion. This is especially critical when dealing with lamellar nanoparticles with a layered structure. The layered structure consisting of a multiplicity of platelets needs to be exfoliated in order to obtain good dispersion. Use of filler within the solution may affect different properties of the solution. The filler particles may, for example, act as charge carriers, and they may interact with solvent, with polymer or with both. These interactions may alter the viscosity and, thus, either improve or impair the fibre formation and the electrospinnability of the solution.

Nanoclay can be used to enhance the mechanical properties of electrospun fibres and they can also increase the surface area of electrospun fibre web, since some of the nanoparticles accumulate on the fibre surface. In a study presented in Paper II we made PVA and PA66 nanocomposite fibres with MMT using two methods for the preparation of the composite. In the first method components were mixed with the solvent to form solution. The second method was *in-situ* polymerization in the presence of MMT, and the solution for electrospinning was prepared using premixed composite. Interactions between the components of the solution, which affected the viscosity, depended on several factors. MMT coordinates well with water and when MMT was allowed to fully delaminate in water before the addition of PVA, the viscosity of the solution was higher compared to the solution in which PVA had been dissolved before the mixing of MMT. This phenomenon was not observed with mixed PA66/MMT composites because the MMT coordinates poorly with formic acid. The viscosity of the mixed PVA/MMT solutions increased when the polymer-to-filler ratio was increased. The viscosity was also found to be dependent on pH, which was most likely caused by the alkaline nature of MMT. Incorporation of functional groups into PVA and organomodification of the clay also changed the interactions between polymer and MMT, which also occasionally affected the electrospinnability of the composite solutions.

The electrospinning process of PVA and PA66 solutions containing MMT did not significantly deviate from those of neat polymers, and fibres were obtained with several solutions (see examples in Figure 17). Composites prepared using a mixing method with unmodified PVA formed even fibre deposition, while mixed composites from functionalized PVA as well as *in-situ* polymerized PVA/MMT composites formed discontinuous depositions. Silanol functionalized PVA/MMT composites also occasionally gelled, which prevented the electrospinning in some cases. Mixing of organomodified MMT with PA66 led to discontinuous deposition in electrospinning, while polymerization of PA66 in the presence of organomodified MMT failed completely. Unmodified MMT, on the other hand, led to even deposition when mixed and also when *in-situ* polymerized with PA66. When electrospinning was successful and fibres were obtained, the nano-sized filler was dispersed through the fibrous network, regardless of the composite preparation method. However, when solution was prepared from premix composite the clay particles within the fibres were smaller compared to those in the mixing method. *In-situ* polymerization, thus, led to better exfoliation and dispersion of the filler.

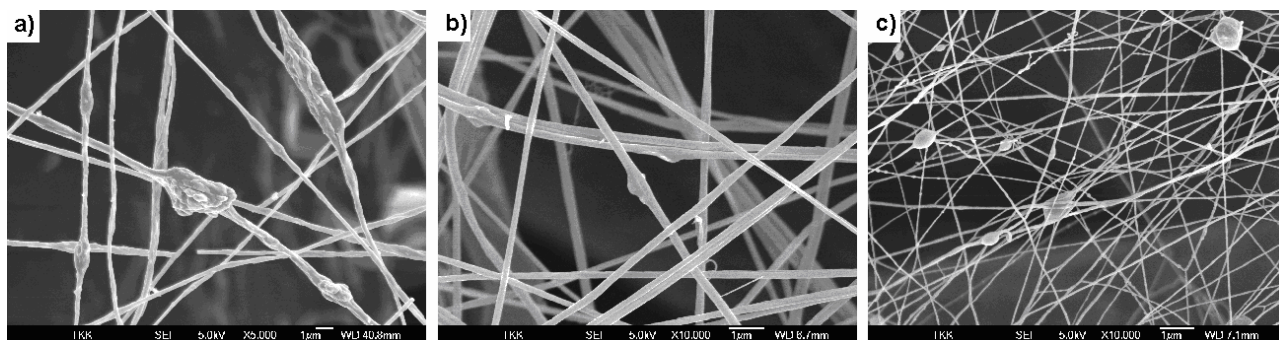


Figure 17. The appearance of the nanofibres containing nanoclay. a) Functionalized PVA containing organomodified MMT; b) In-situ polymerized PA/MMT composite; and c) PA66 containing organomodified MMT.

Contact angle and water penetration measurements were conducted on substrate surfaces coated with PA66/MMT composite fibres. The more hydrophobic organomodified MMT produced more hydrophobic surfaces than the hydrophilic, unmodified MMT. Better dispersion of nanofiller within the fibres, obtained with *in-situ* polymerization method, led to a more hydrophilic surface compared to fibres prepared by the mixing method.

In a study published outside the papers of this thesis, nanofibres containing a high amount of TiO_2 were prepared using PEO as a carrier polymer [55]. The filler content of the solution was as high as 27.5 wt%, and polymer content was only a fraction of that. In examples presented in Figure 18, the polymer concentration of the solution changed from 1 wt% to 5 wt%, and polymer content of the nanostructures varied, thus, from 3.5 wt% to 15.4 wt% respectively.

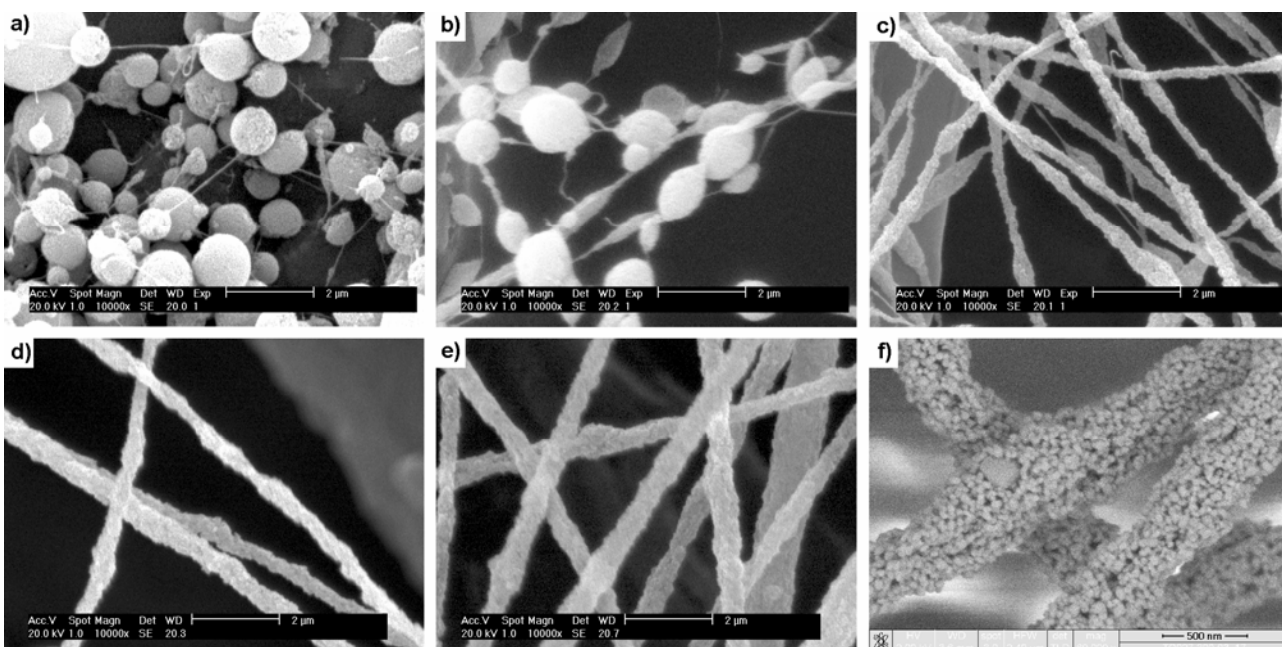


Figure 18. Change in morphology from beaded fibres to bead-free fibres of TiO_2 /PEO with increasing polymer concentration: a) 1 wt%, b) 2 wt%, c) 3 wt%, d) 4 wt%, e) and f) 5 wt%. TiO_2 content of all solutions was 27.5 wt%.

A mainly fibrous structure was obtained when the polymer concentration in the solution was 3 wt%, which corresponds to a polymer content of 9.8 wt% within the fibres. The surface roughness and slightly varying

diameters is caused by the filler. The *change in morphology* from beaded fibres to bead-free fibres can be clearly seen in fibres with increasing polymer concentration. The lack of chain entanglements led to incomplete fibre formation and beaded structure, regardless of the viscosity of the solution. For example, the viscosity of the composite solution containing 2 wt% of polymer was 244 cP, which typically is enough for fibre formation with neat PEO solution, but led now to a beaded structure. The formation of bead-free fibres did not occur until the polymer concentration, which provided the chain entanglements into the solution, was high enough for bead-free fibre formation

In summary, the electrospinning is a suitable method for nanofibre production from many neat polymers that are soluble in some common solvent, but different systems are also possible. We demonstrated the use of self-organizing co-polymer in electrospinning. When fibre formation was followed by the selective removal of one component we obtained a uniform porous structure throughout the fibre. The preparation of composite fibres was demonstrated using nano-sized clay and TiO₂ as fillers.

A binary solution presents a typical *change in morphology* with increasing polymer concentration. This *change in morphology* starts from separate droplets to beaded fibres and to smooth fibres, then to larger fibres and to ribbon-like fibres until the jet formation is inhibited due to the immobility of the highly entangled polymer chains. The operating window of fibre formation for the specific polymer-solvent system might be slightly shifted by varying process parameters such as voltage. This is because the voltage and polymer concentration have an opposite effect on the process and on the formation of fibres, since the concentration promotes the stability and the voltage promotes the instability of the jet. The electrospinning parameters need to be optimised to each polymer-solvent system separately since many variables affect the fibre diameters, the fibre diameter distribution as well as the evenness of the nanofibre web, and there are no universally applicable laws of electrospinning.

Additives and fillers of many kinds can be incorporated into electrospun nanofibres. When additive or filler is introduced into polymer solution, it increases the possibility of different kinds of interaction within the solution. Nano-sized filler can be used to form composite fibres. The interactions occurring in the presence of filler particles may have an effect on the viscosity or the other properties of the solution. The electrospinnability of the solution may also be changed due to these interactions, but it may also remain intact, regardless of the additive. The typical *change in morphology* appearing with neat polymer-solvent systems may also be observed with composites as was observed with our TiO₂ composites. In contrast, increased interactions may lead to other phenomena such as gelation of the solution, which may prevent the electrospinning process. This kind of behaviour was observed with some of our MMT composites. Some additives or fillers may act as charge carriers in solution. Charge carriers such as salts or nano-sized clay have an influence on the conductivity of the solution, and they may promote two phenomena having opposite effects on the fibre formation and diameters. They may, firstly, increase flow rate, which can lead to larger fibres, and secondly, increase Coulombic repulsion, which can lead to smaller fibres. The optimization of process parameters for ternary systems can be even more challenging than for binary systems.

7 Formation of Nanofibre Composite Layer

In most of our trials one aim was to achieve an even distribution of nanofibre coating on the substrate surface, but the formation of coating and variables affecting the evenness of the coating were the special interest in a study presented in Paper IV. The idea for the study arose from findings that electrospinning typically yielded round depositions, in which the fibre amount often varied in circular regions as presented in Figure 6 on page 15. Electric field of the electrospinning process was modelled for better understanding and controllability of the fibre formation and deposition. We discarded the modelling study of single fibre formation and its dynamics in the electric field since the topic has already been widely studied [39-42, 45, 210-211, 274, 385-388]. The modelling of the steady-state conditions of the electric field appeared to be more important for the filtration material quality.

The preparation of filtration material also necessitates the scaling-up of the process and preferably also high productivity per nozzle. The scaling-up can be done using a large number of nozzles [496-497] even though a nozzleless design can also provide larger deposition and higher productivity [35, 342]. The use of uniform nozzles leads to more uniform fibre diameters, which favours the use of nozzles especially when preparing nanofibre web for a filtration application. A multi-nozzle design was, therefore, employed in this thesis in order to obtain large webs.

Results of modelling are discussed in Chapter 7.1, trials with more than one nozzle and the construction of a multi-nozzle electrospinning design are discussed in Chapter 7.2, and issues concerning the production rate per nozzle are discussed in Chapter 7.3.

7.1 *Modelling of Electrospinning*

The effects of the two main process parameters, voltage and distance, on the electric field were studied in Paper IV using modelling (see Chapter 5.3.2). The basis of the model was eSp1 equipment (predecessor of eSp2) and the parameters of the basic model were those that produce an even fibre coating with the 10 wt% PVA solution; a distance of 150 mm and a voltage difference of 40 kV, divided between the nozzle (20 kV) and the collector (-20 kV). The distributions of the overall electric field of the basic model at different distances from the nozzle are presented in Figure 19. In the first frame the observation plane is touching the tip of the nozzle so the distance from the plate is 150 mm. In the following frames the plane is moved towards the collector plate. The highest field strength is expressed with a red colour. In the vicinity of the nozzle the effective electric field is round. The effective field widens towards the collector and reformates into a square shape in the vicinity of the plate. The round shape of the nozzle dominates the shape of the electric field at over half the distance towards to the collector.

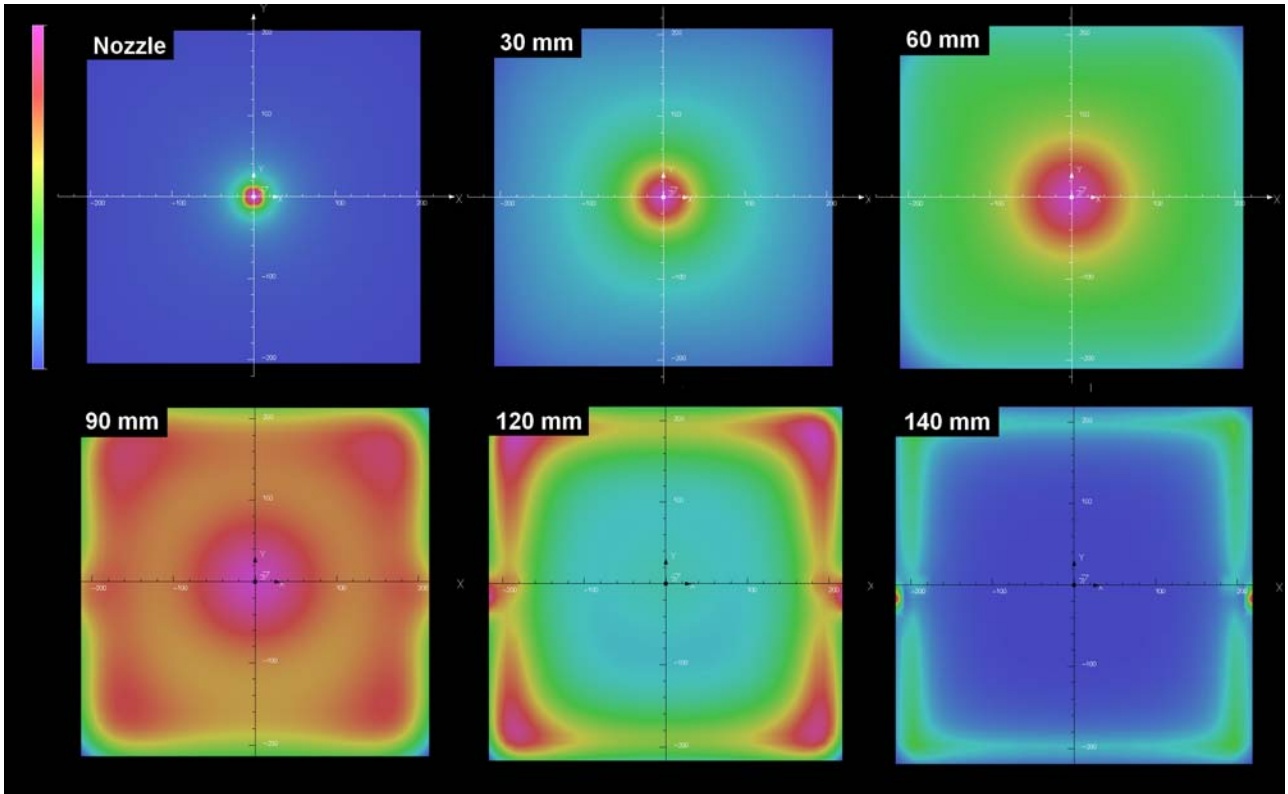


Figure 19. Overall field distribution of the basic model in different parts of the electric field. The observation plane is first touching the tip of the nozzle and then moved to different distances from the nozzle. Since the distance between the nozzle and the collector is 150 mm, the last frame presents the field 10 mm from the plate.

The variations made to the model can be divided in three groups. Firstly, the voltage was varied while the distance was fixed. Secondly, the distance was varied while the voltage was fixed. And thirdly, the effect of the average electric field strength was studied comparing three arrangements, where both distance and voltage were varied. There were no differences between the E_x and E_y components in the models due to symmetry of the system. E_x and E_y widen the path of the jet away from the centre line. The E_z -component, which pulls the jet towards the collector, was the most dominant of the field components. Its values were one or two orders of magnitude higher than values of E_x and E_y components. The field components were not constant along the observation line, which explains the fibre quantity variation in circular regions. It might also alter fibre diameters in different parts of the coating. In the vicinity of the nozzle all of the components were increased: the widening E_x and E_y component, and the pulling E_z component. Increasing voltage increased the magnitudes of the field components and strengthened the field, but the shape of the field remained the same. E_x component is presented in Figure 20a as an example.

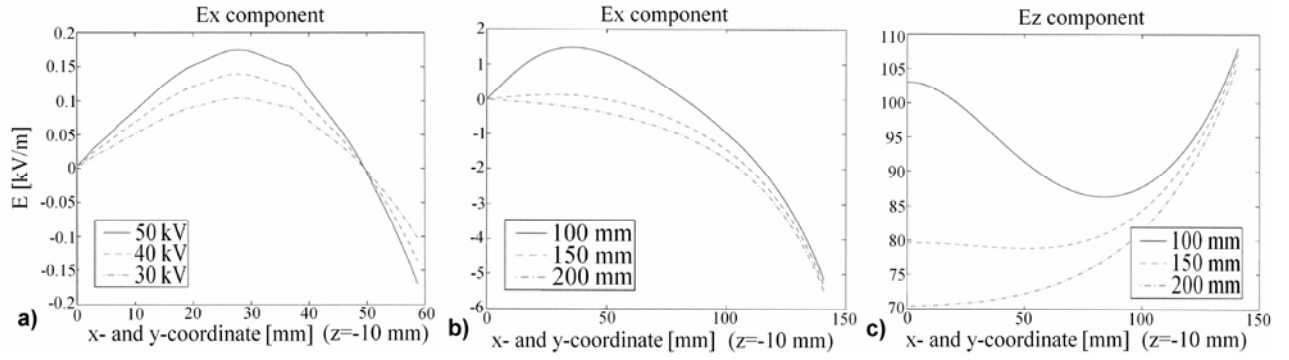


Figure 20. a) Effect of changing voltage on the strength of the E_x component, b) Effect of changing distance on the strength of the E_x component, and c) Effect of changing distance on the strength of the E_z component. x - and y -coordinate in x -axis indicates the position of the observation point in the observation line (see Figure 13 in page 48).

Increasing distance weakened the electric field. However, in the calculated models it was not possible to compensate this weakening by increasing the voltage. This is because the change in distance also changed the shape of the electric field, as can be seen from both the E_x and E_z components presented in Figure 20b and Figure 20c, respectively. Thus, the distance determined the overall nature of the electric field. Long distances yielded a more homogenous electric field, which is advantageous for the evenness of the coating. A small distance caused the E_z component to rise near the centreline that can explain the bull's eye shape sometimes observed in electrospinning trials.

In addition to the one-nozzle basic model, three multi-nozzle models were also studied and published outside the papers of this thesis [288]. These multi-nozzle models included two nozzles aligned vertically one above the other, two nozzles aligned horizontally side-by-side, and six nozzles in a 2×3 grid. In all cases the internozzle distance was 25 mm. The field components of the multi-nozzle models and the basic one-nozzle model are presented in Figure 21. There was no difference in the strengths of the field components between the horizontal and the vertical two-nozzle arrangements. The levels of the field components in the multi-nozzle models were higher than those of the basic model, the six-nozzle model having the highest values. The positive part of the E_x component was increased, suggesting a widening of the deposition when multiple nozzles were applied.

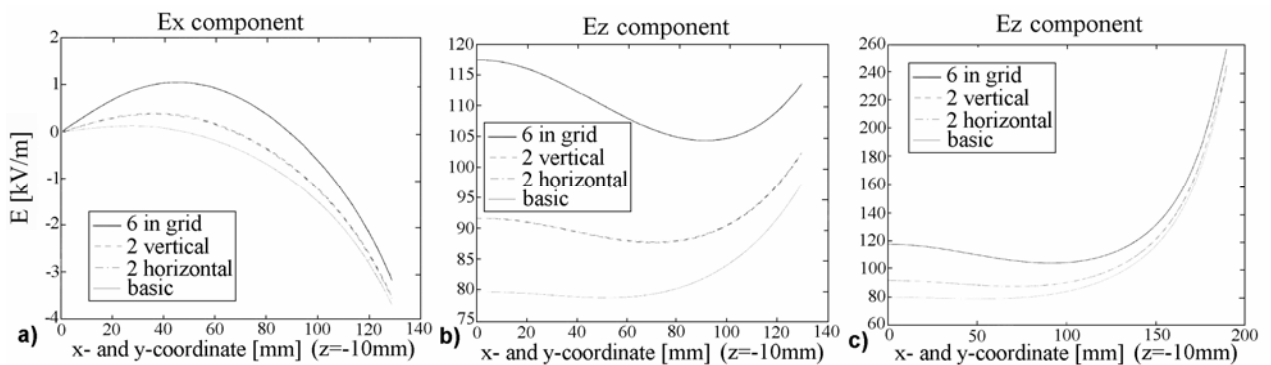


Figure 21. Field component E_x (a), and component E_z (b & c) of the multi-nozzle and basic models. Multi-nozzle models are two nozzles vertically aligned and horizontally aligned and six nozzles in a grid.

These models did not take into account, for example, the viscous forces of the jet, or the mutual repulsion of the jets charged with the same polarity. These affect the electrospinning process, and the model did not explain all the observations made in trials. The model did, however, provide valuable information about the shape of the field and phenomena of the electrospinning process.

7.2 Electrospinning with Multiple Nozzles

Typical laboratory scale electrospinning equipment consists of one nozzle and a collector plate. If the electrospinning process occurs optimally, this kind of arrangement leads to a deposition pattern round in shape [159]. In the case of multi-jetting, mode deposition can also consist of several round patterns [342]. The shape of the plate does not have a major influence on the deposition pattern. In the case of eSp2 equipment with square a collector plate, for example, polymer jet forms a round and usually relatively large deposition pattern on substrate, the size of which depends on the polymer used. Circular patterns are often obtained in addition to even round depositions. In Paper IV the circular deposition of PVA was observed with low electric field strength, while, for example, unreported trials carried out with PAN solution produced circular depositions more easily when the strength of the electric field was high. The diameter of the deposition pattern can be as large as twice the distance, but typically it is smaller [Paper IV, 159]. The diameter of the PA66 deposition, for example, was approximately 350 mm with distance of 300 mm [Paper III]. The diameter of PVA deposition pattern was found to increase with increasing distance and increasing voltage; the largest deposition pattern, having a diameter of over 300 mm, was obtained with voltage of 80 kV over a distance of 200 mm [Paper IV]. In order to obtain a larger coated surface with electrospinning a multi-nozzle design is needed.

A two-nozzle design has been demonstrated outside the papers of this thesis with eSp2 [288] using aqueous solution of PVA (Merck) and two nozzles arranged side-by-side. When the internozzle distance was longer than the diameter of the deposition pattern, two round separate deposition patterns were formed. When the nozzles were brought closer together the deposition patterns started first to flatten from the facing sides, and then to merge. The PVA jets were not repelling each other notably. When the internozzle distance was less than 25 mm, the nozzles interfered with each other and the production rate decreased considerably. The merging of two deposition patterns is not, however, typically the case; usually jets from adjacent nozzles repel each other [393]. We have observed repelling in unreported studies with PA, PEO and PAN. The formation of the separate deposition patterns must be taken into account when multiple nozzles are used in electrospinning.

Nozzles can be arranged into different arrays. Arrays can be, for example, arc shaped or the nozzles can be arranged in different kinds of matrix [496]. Our approach in multi-nozzle eSp3 equipment is the use of tubes so that the nozzles are forming straight rows (see Figure 10b and c in page 45). The jets from adjacent nozzles normally repel and restrict each other's whipping, and therefore they are not only pushed away from each other, but the vicinity of other jets can also change the shape and size of the deposition patterns [393]. Thus, it is not surprising that the deposition pattern of eSp3 from one tube is a row of vertically elongated ellipses. The envelope cones and the ellipses of the outermost nozzles of the tubes are wider than those in

the middle, since they have a restricting jet on only one side (see Figure 22). The distances of the centre points of the ellipses are larger than the internozzle distance, and the size of the ellipses is smaller than the size of deposition pattern obtained with the same solution in eSp2. When the web is moving in eSp3, ellipses form stripes onto web. The width of the stripe can be as small as 10 % of the distance.

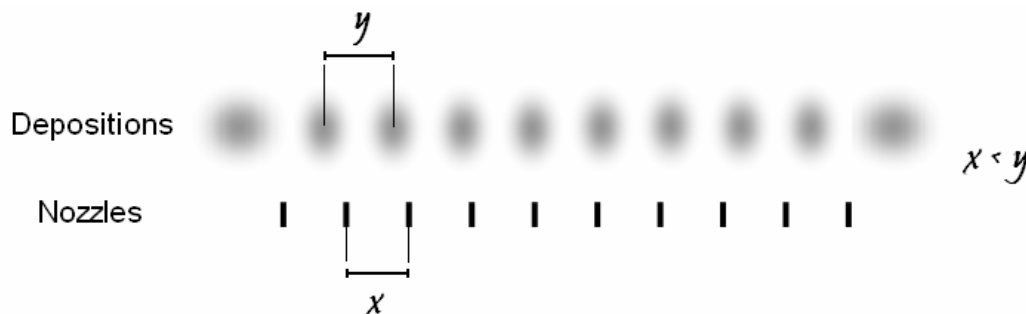


Figure 22. *The row of ellipse-shaped depositions from one tube.*

In order to obtain full coverage of nanofibres on the moving substrate several tubes are needed. They can be attached on top of each other on the rack (see Figure 10 on page 45). It seems advisable to arrange the tubes in pairs in a staggered alignment. In this alignment the vertical shift between the tube pair is half of the internozzle distance (see Figure 23a). In this arrangement the nozzles of two tubes form a regular saw-like pattern and the repulsive forces affecting each jet, excluding those at the end of the tubes, are identical. When the web is moving, the stripes of the second tube usually cover the gaps left by the stripes from the first tubes. Full and even coverage is easier to obtain when the deposition pattern from one nozzle is even instead of circular since the circular pattern highlights the edges of the stripes (see Figure 23b and c). If the electrospinnability of solution is poor and formation of continuous deposition fails, as in the case of some polymer/nanoclay solutions in Paper II, the scaling-up is not feasible with nozzles. If the jetting mode is not stable, some wobbling of the stripe can occur, which can also cause unevenness of the coating. In order to obtain full coverage of the web or increase productivity, a second tube pair can be included. Its nozzles are now arranged into a staggered alignment with the first tube pair in order to ensure evenness. The second tube pair is located separately as presented in Figure 23a in order to avoid dissymmetric repulsion between tube pairs. More tubes can be included using the same principles in order to increase production rate or improve the evenness of the coating further. PA6 was used in wide parameter study conducted using continuous eSp3 equipment [Paper VI]. The study was carried out using two tubes.

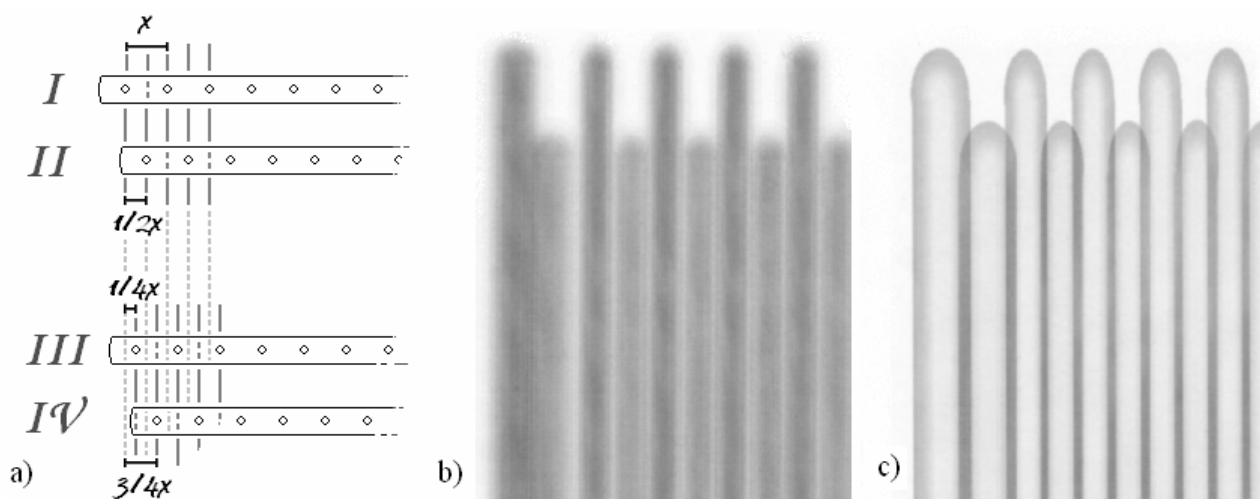


Figure 23. a) Staggered alignment of four tubes as two tube pairs (x is the internozzle distance). Coverage obtained with two tubes with even (b) and circular (c) deposition pattern.

7.3 Production Rate per Nozzle

Process parameters as well as the properties of the polymer solution affect the production rate of one nozzle. The flow rate of the solution corresponds to the productivity when the electrospinning process is optimal and the entire solution forms fibres instead of dripping from the nozzles. The flow rate depends, for example, on the nozzle size, the strength of the electric field and the viscosity of the solution, but it can also be controlled by a type of solution feeding system. The fibre formation speed is also influenced by the strength of the electric field and the viscosity of the solution, but also by other solution parameters, such as the amount of the charge carriers. A study presented in Paper VI examines the effect of several parameters, including both the solution and the process parameters, on the productivity of the electrospinning of PA6. The mean effects of different levels of each parameter are presented in Figure 24. The main parameters affecting the productivity were the strength of the electric field and its factors, the distance and the voltage. The effects of the PA6 grade and the formic acid grade were, on the other hand, negligible.

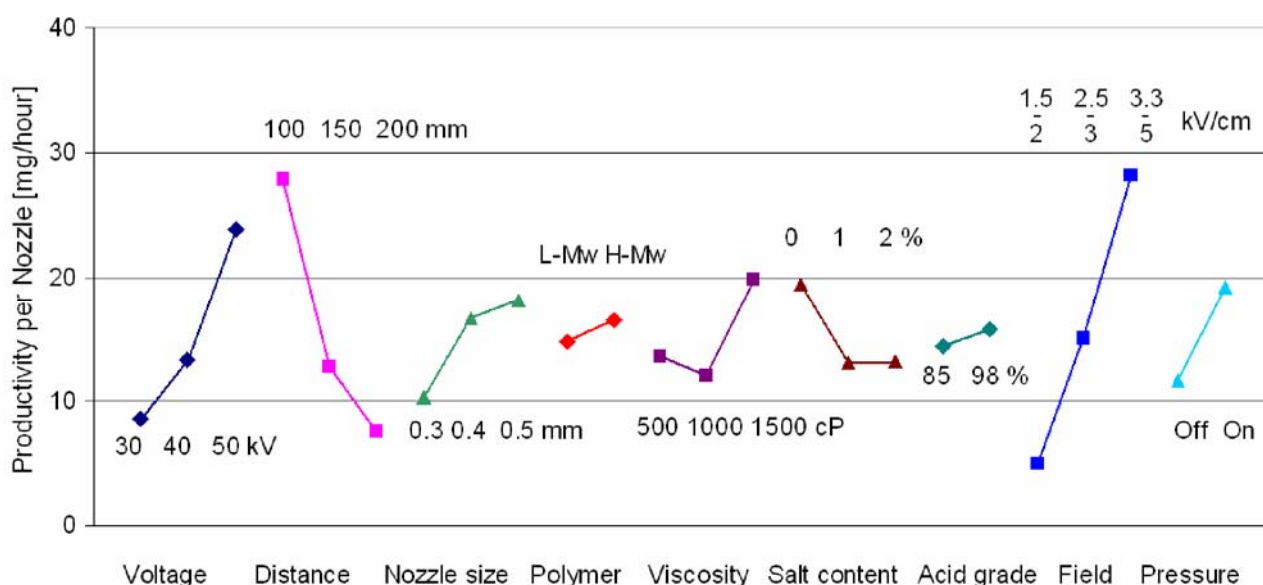


Figure 24. Mean effect of the selected process and solution parameters on productivity per nozzle.

Productivity was directly proportional to nozzle size, voltage, and strength of the electric field. Large nozzles enable large mass flow, which also seemed to be enhanced by the increased voltage and the increased strength of the electric field. Therefore it is not surprising that productivity was inversely proportional to the distance, but the reverse relationship was also observed with salt content. In general, salt increment has been found to increase [281, 327] as well as decrease productivity [237]. Different salts with different chemistry and molecule size can act in different ways [137, 411], and use of some other salt than potassium formate might have had a beneficial effect on productivity. The dependency curve between productivity and viscosity was concave in shape. The highest viscosity was associated with the highest productivity, which is probably partly due to the increased fibre diameter (Figure 15 in page 50) and thus increased mass flow. The lower range of viscosity might, on the other hand, favour the lengthwise production rate of fibres due to the higher mobility of the more dilute solution. This was considered to be the explanation for the concave shape of the curve. Use of feeding pressure yielded higher productivity than the unpressurized feeding of the polymer solution.

The effect of PA6 grade on productivity was negligible, but with different polymers the situation is quite different, even within the same polymer group. Paper VI investigated the productivity of electrospinning with various polyamides. The solution consumption (ml/min) was determined for PA6, PA66, PA612 and PA614 in order to evaluate the fibre production rate of one nozzle (g/h). The consumption determination of the PA1012 and PA1014 solutions failed due to too rapid stagnation of the solution in the nozzle while cooling. The measured productivities (g/h) are presented in Figure 25 together with fibre diameters (nm). Fibre diameters of PA66 and PA612 were smaller and the fibre production rates higher than that of other polyamides, so the increase in productivity must be due to the higher fibre formation speed and not only the result of higher mass flow.

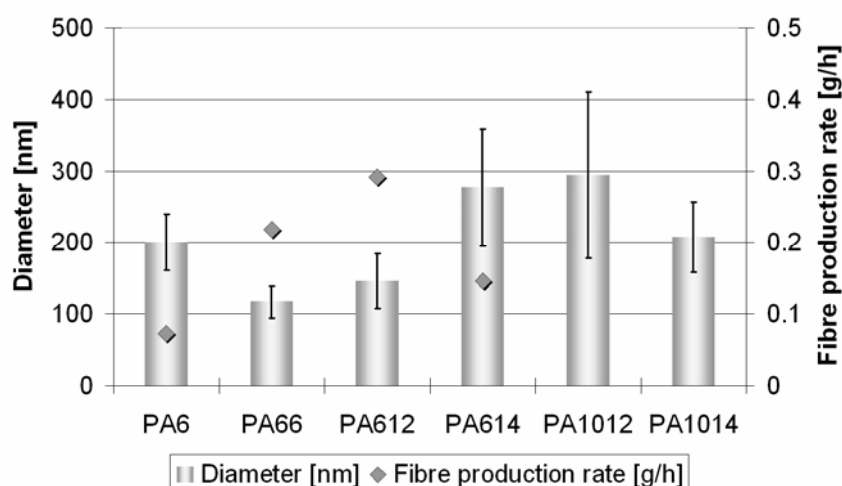


Figure 25. Fibre diameters with standard deviation and fibre production rates of different polyamides.

The fibre production rate of the electrospinning system utilizing nozzles may be retarded due to process problems such as dripping of the solution and blocking of the nozzles. In a parameter study presented in Paper VI dripping and blocking were observed. From all studied parameters only pressure had a clear and significant effect on dripping. Other parameters had smaller or larger arbitrary effects on the occurrence of

process problems. In trials outside of the papers of this thesis, it was found that such problems seemed to accumulate. When the solution was dripping, the blocking tendency of nozzles was also higher compared to a stable situation when the entire solution was consumed in fibre formation. Dripping can be reduced by increasing the viscosity of the solution or reducing the flow rate. The reduction of flow rate in the case of eSp3 involves the use of smaller nozzles or reduced feeding pressure. Increase in viscosity is usually achieved by increasing the polymer concentration, which may increase the blocking tendency of the nozzles [5, 240, 242]. Depending on the polymer-solvent system used, the gas or vapour climate around the nozzles may reduce the blocking tendency [323, 494]. In the case of PA6/formic acid system, the water vapour was found to reduce the blocking tendency and continuous operation has been carried out in a moist climate for eight hours with no indication of nozzle blocking. However, in the case of PAN/dimethylformamide the effect of water vapour was reversed leading problems.

In summary, the electric field is essential in the electrospinning process. Its strength is determined by the voltage and the distance, but modelling of the electric field revealed that the overall nature of the field is mainly dependent on the distance. The variation of the voltage only varied the levels of the overall field strength and the directional components of the field, but the variations of the distance changed the shapes of the curves presenting the directional components of the field in the different parts of the electric field. The increased amount of nozzles widened the effective field in the model though in practice the multi-nozzle design is more complicated due to mutual repulsion between the jets from adjacent nozzles. The multi-nozzle design needed for the production of larger webs can be practically constructed using nozzle tubes. The tubes can be arranged in pairs in a staggered alignment in such a way that the vertical shift between the tube pair is half of the internozzle distance. This ensures that identical repulsion forces are acting on each jet with the exception of the outermost ones. Additional tube pairs can be added in staggered alignment with the first one in order to ensure full coverage, enhance the evenness of the coating and increase productivity.

8 Nanofibre Composite in Filtration

Electrospun nanofibres, having small fibre diameter, high porosity and other specific properties, are considered advantageous for filtration applications [8, 18, 22, 32, 53, 68]. ULPA requirements are also achievable with glass fibres, but the material leads to a risk of loose short fibre, which should not be the case with the continuous polymeric nano fibre. Additionally, the handling of polymeric nanofibre webs is simpler than that of the glass fibre webs. Besides filtration properties, there are also other properties of electrospun fibres that are interesting from the filtration point of view. These properties include, for example, fibre diameters, surface area of the materials, fibre diameter distribution, pore size as well as thickness and mechanical strength of the nanofibre layer. These properties of electrospun fibres are studied in all papers and the filtration properties of nanofibre layer was the main topic of Paper III, and was also studied in Paper V. Structure and mechanical properties of fibrous web are discussed in Chapter 8.1, and the filtration efficiency and the pressure drop of the nanofibre coated samples are discussed in Chapter 8.2.

8.1 *Properties of the Fibrous Web*

Small fibre diameter is advantageous in filtration. The slip-flow effect, which enhances filtration efficiency and reduces the pressure drop, occurs when fibre diameters are around 500 nm or below [32, 187]. Small fibres are obtained with low polymer concentrations, but low concentration typically also promotes the occurrence of beads, which might reduce the strength of the fibres. The mechanical strength of small, bead-free fibres is also limited. Polyamides have good mechanical properties, such as high tensile and impact strength, and abrasion resistance [503], and they have been found to be suitable nanofibre material for filtration applications [27, 30, 34, 54, 57, 59-60, 63-67].

Preparation of electrospun PA fibres is reported in Papers III, V and VI. Bead-free electrospun PA66 fibres had mean fibre diameters slightly above 100 nm with a relatively small fibre diameter distribution. The mean fibre diameters of PA6 were typically below 200 nm, but it was influenced by several solution and process parameters [Paper VI]. PA612 also produced fibres with mean diameters clearly below 200 nm. The diameters of PA614, PA1012 and PA1014 fibres had mean diameters in the range of 200 nm to 300 nm [Paper V]. Even though all of these studied polyamides have proven to be generally feasible for electrospinning, the better electrospinnability and the higher production rate of so called lower polyamides, PA6 and PA66, made them a better choice for commercial filtration applications. Electrospun fibres of water-soluble PVA can also be used in filtration membranes after cross-linking [76]. PVA fibres in Paper IV had mean diameters ranging from 500 nm to 800 nm. Electrospun PA/MMT composite fibres in Paper II had diameters of around 100 nm, but they also contained occasional nanoclay agglomerates with larger diameters of micrometer scale. The diameter of the self-organized fibres in Paper I typically ranged from 200 nm to 400 nm.

Surface area of fibrous filter material depends on fibre diameters, but also on other factors. The surface area of the electrospun fibres may be increased in several ways. One frequently reported characteristic of electrospun fibres is surface porosity [259, 331-332], whose occurrence is associated, for example, with

solvent evaporation. Increase of surface area may also be caused by artefacts protruding from the fibre surfaces. In Paper II nanoparticle agglomerates with a larger diameter than the fibres form bulges, and in Paper VI globule-like artefacts on the surface of the fibres occurred occasionally with solutions containing salt. Nanoweb structures of smaller fibres between the nanofibres forming the continuous web were also observed in Paper VI. The most effective way of increasing the surface area within this thesis is still found in Paper I. The use of the self-organizing block-co-polymer amphiphile system and the selective removal of one component from the fibre structure led to porous structure with pores extending to the fibre core, not just on the surface layer.

Pore size of electrospun layers depends on the amount of fibres. In Paper III samples having different amounts of PA66 nanofibre coating on different textile substrates were prepared for filtration efficiency measurements. The nanofibre layers had coating weights of 0.02 g/m^2 , 0.1 g/m^2 , and 0.5 g/m^2 . The approximated thicknesses of the nanofibre layers were $0.52 \text{ }\mu\text{m}$, $2.60 \text{ }\mu\text{m}$, and $13 \text{ }\mu\text{m}$, and the average pore sizes 1190 nm , 540 nm , and 260 nm , respectively. The interdependence between the porosity of the filtration layer and the amount of nanofibres can be seen in Figure 26. The slight elongation of the samples affected the shape of the pores in the nanofibre layer, but the average pore sizes of the samples remained in the same range as unstrained samples. Since the pore size remained at the same level, it can be assumed that if a nanofibre layer is not broken, its filtering efficiency will not change markedly due to the slight elongation.

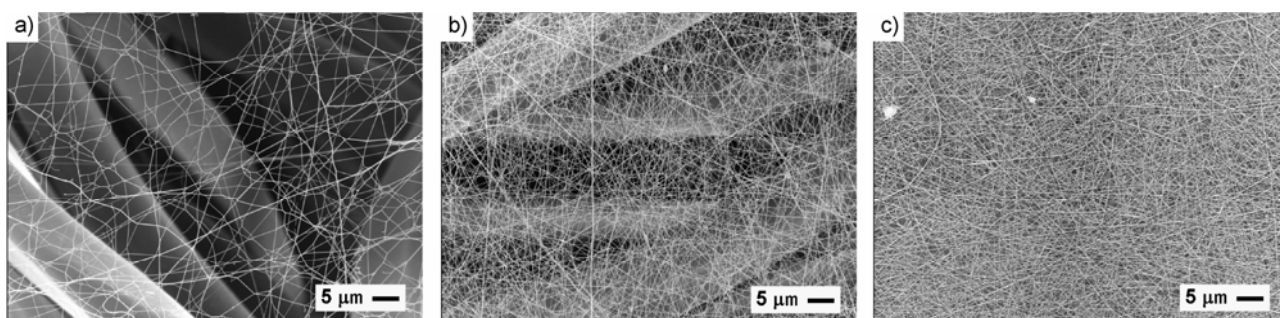


Figure 26. SEM pictures of coated knitted fabric samples with coating weights of a) 0.02 g/m^2 , b) 0.1 g/m^2 , and c) 0.5 g/m^2 .

Elongation tests presented in Paper III (also [464]) also revealed the limited mechanical strength of the electrospun PA66 nanofibre layers. The strain capacity of the thinnest 0.02 g/m^2 layer was less than 30 %, and one of the thickest 0.5 g/m^2 layer only less than 10 %. Whereas the thickest coating delaminated, the lighter coatings ruptured in many places and small pieces of coating remained on the textile surface. The elongation capacity of the nanofibre layer depends on many factors including 1) the nanofibre elasticity, 2) the number of entanglements in the nano-scaled nonwoven structure related to the layer thickness, 3) the number of attaching points on the substrate, and 4) the morphology, mainly the coiling pattern of the nanofibre on the substrate. Therefore it is natural that the fibre layer will lose its elongation capacity when the thickness of the layer is increased. Due to the limited strain capacity and the delamination propensity, the electrospun nanofibre layer should preferably be used with a relatively rigid substrate, which can also act as a coarse filter. It is advisable that at least thick nanofibre layers are protected with the cover layer. In addition to the large ruptures and the delamination also smaller, micro-sized damage in the nanofibre layer can

occur. This can be caused, for example, by filtered aerosol particles. Images of the different kinds of damage to the nanofibre web are presented in Figure 27.

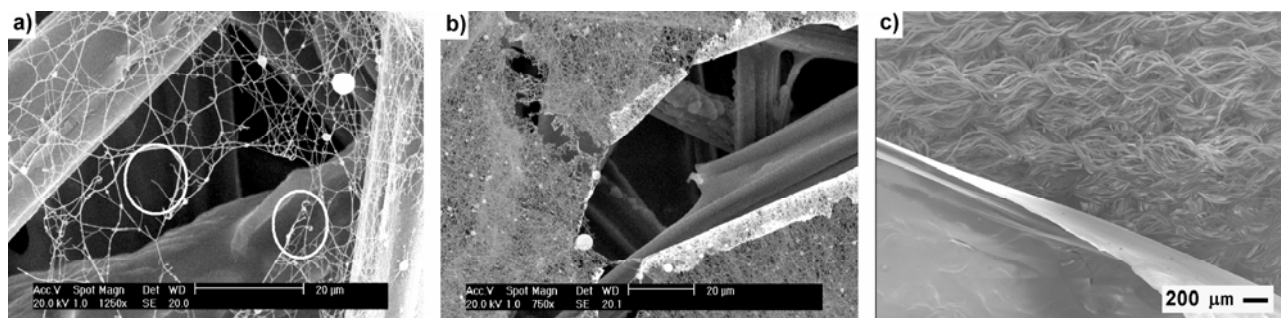


Figure 27. a) Micro-breach in nanofibre structure with free fibre ends around it, b) larger mechanical damage in nanofibre web, and c) delamination of the nanofibre web due to elongation of the substrate.

The strength of individual fibres may be increased using nano-sized filler as reinforcement. Use of nano-sized clay has been discussed in Paper II and in Chapter 3.2, but the evaluation of mechanical properties of the layers was outside the scope of the paper. Incorporation of nano-sized clay into spinning solution and obtaining good dispersion of intercalated clay lamellas within the electrospun fibres is challenging, but achievable [239, 427]. Clay may also affect the hydrophobicity of the nanofibre layer. Nanoparticles can also be used in order to obtain functionality in filter fibres, TiO_2 for example can be used in photo catalytic filters [55]. In a study reported outside the papers of this thesis, but reported in Chapter 3.2, anatase TiO_2 was included in PEO solutions of different concentrations. Composite solution produced nice fibrous structures in electrospinning, when PEO content in solution was 3 wt% - 5 wt%. Polymer content of the fibre was 9.8 wt% - 15.4 wt%, respectively. The photo catalysis will eventually decompose the organic polymer matrix from the fibres. Cohesion of fibre consisting only of TiO_2 after oxidation of polymer was not studied, but the initially low polymer content suggests that the structure might be quite stable anyway.

8.2 Filtration Efficiency

In a study presented in Paper III (also [54]), the filtration efficiency of the fibrous substrates with PA66 nanofibre layers was measured using particles with a size range of $0.12\ \mu\text{m}$ - $5\ \mu\text{m}$. The filtration efficiency clearly increased even with the lowest amount of nanofibres ($0.02\ \text{g/m}^2$) compared to uncoated samples. With the highest nanofibre coating weight ($0.5\ \text{g/m}^2$) the filtration efficiency of the sub-micron aerosol particles was over 90 %. The level of the pressure drop caused by the nanofibre layer of all tested materials remained at an acceptable level for most applications and the pressure drop with the highest coating amount varied from 124 Pa to 214 Pa depending on the substrate material.

The ability of nanofibres to capture the smallest air borne particles is better than that of larger fibres [187]. Therefore, in Paper V the filtration efficiency was tested using sub-micron particles ranging from $0.16\ \mu\text{m}$ to $0.94\ \mu\text{m}$. The results of the filtration efficiency measurements are presented in Figure 28a. The measurements were conducted on samples containing electrospun layers with different amounts of PA66 nanofibres varying from $0.01\ \text{g/m}^2$ to $1\ \text{g/m}^2$ on nonwoven substrate using air flow velocity of 10 cm/s. The filtration efficiency of uncoated nonwoven substrate ($0\ \text{g/m}^2$) was less than 10 % regardless of the particle

size. Even an amount as low as 0.01 g/m^2 of nanofibres had a notable effect on the filtration efficiency. The rise of filtration efficiency was faster with particles having diameters above $0.5 \text{ }\mu\text{m}$, but the efficiency of smaller particle range, where conventional microfibre filters have their MPPS [500], also increased. The nanofibre coatings of 0.1 g/m^2 and 0.2 g/m^2 increased the filtration efficiency of the smallest particles used in the determination ($0.16 \text{ }\mu\text{m}$) to around 60 % and 80 %, while the pressure drop of the samples remained below 100 Pa. The filtration efficiency of 0.5 g/m^2 coating was 95 % or above regardless of the particle size, and with the larger particle size of $0.73 \text{ }\mu\text{m}$ the efficiency was over 99 %. Increase of coating weight above 0.5 g/m^2 failed to improve the efficiency, but rather had an adverse effect when the pressure drop increased to an unusable range. The pressure drop was quite linearly dependent on the coating thickness (see Figure 28b).

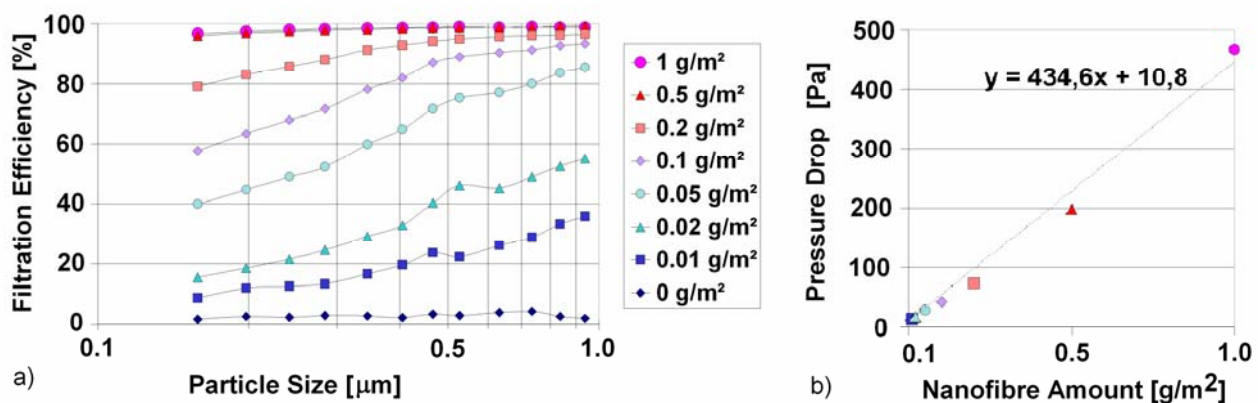


Figure 28. The filtration efficiency (a) and the pressure drop (b) of uncoated and PA66 nanofibre coated nonwoven samples.

Electrospinning utilizes electrostatic forces, and electrospun fibres can carry residual charges [7, 57]. Residual charges occur especially when the polymer used is highly insulating and charge dissipation is difficult and slow. These residual charges can enhance the filtering efficiency of the electrospun material due to electrostatic attraction [187]. The effect of possible residual charges on the filtration efficiency of PA66 nanofibre layer was studied in Paper III by removing residual charges from samples with isopropanol. Figure 29 compares the efficiency of two samples before and after isopropanol treatment.

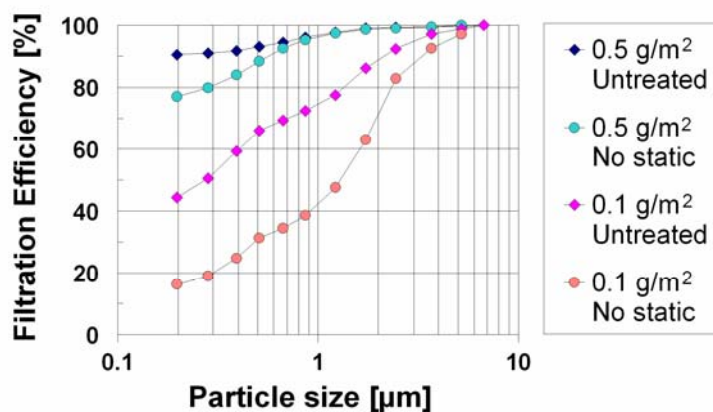


Figure 29. Filtration efficiency of untreated and isopropanol treated static free samples.

The filtration efficiency of the treated non-static samples was lower than the efficiency of the untreated samples with smallest particle ranges and with lower coating weight (0.1 g/m^2). This decrease in filtration efficiency can, however, be caused by the observed damaging of the nanofibre layer during the isopropanol treatment. With a more durable sample, having higher coating weight and with coarse particle range, no effect was discernible.

In summary, many polymeric materials are suitable for aerosol filtration applications, and the small fibre diameters that enable the slip-flow effect are easily achievable with the electrospinning method. The surface area of electrospun fibres can be increased by different means, including protruding artefacts and porosity of fibres, which do not affect the fibre diameters and thus the mechanical strength of the electrospun web. The strength of the nanofibre web depends on many factors, but generally it is advisable to use electrospun fibres as an effective layer on the substrate material. Only a small amount of nanofibres had a notable effect on filtration efficiency. High filtration efficiency of sub-micron particles is achievable with electrospun fibre. This higher efficiency is obtained when the diameter scale of the filter fibres is close to the fineness of the aerosol particles and the specific surface area of the filter media is high. Care must be taken, however, to ensure that the increase in pressure drop does not rise too high. Use of multiple, separate thin layers with high filtration efficiency instead of one thick layer might ease the air flow. Even though electrospun fibres may possess some residual charges that, in theory, might enhance the filtration efficiency, this effect was not pronounced with PA66.

9 Conclusions

Many neat polymeric materials are suitable for aerosol filtration applications. In this study, for example, our PA66 and PA612 grades have good mechanical and chemical properties combined with small fibre diameters and high productivities in electrospinning. Small fibre diameters, below 0.5 μm , are advantageous for filtration applications due to the slip-flow effect. The fibre diameters of the electrospun web depend mainly on the polymer and its molecular weight, but it can be somewhat adjusted by altering the solution and the process parameters. In a parameter study carried out with PA6 and eSp3 design the main parameters affecting the fibre diameters were the viscosity and the salt content of the solution, and the strength of the electric field. Electrospinning also enables the use of filler, which can improve the properties and introduce functionalities to the electrospun fibres. Lamellar nanoparticles such as MMT clay could act as a reinforcement component within electrospun fibres and at the same time they can modify the hydrophobicity of the surface of the material. TiO_2 , on the other hand, can be used to add photo catalytic activity into fibre media.

The typical *change in morphology* appearing with neat polymer-solvent systems may be also observed with composites, as was the case with our TiO_2 composites. The increased interactions occurring within the composite solutions may also cause adverse phenomena, which may prevent the electrospinning process as observed with some of our MMT composites. Some additives or fillers may act as charge carriers in solution. Charge carriers such as salts or nano-sized clay have an influence on the conductivity of the solution, and they may promote two phenomena having opposite effects on the fibre formation and diameters. They may, firstly, increase in flow rate, which can lead to larger fibres, and secondly, increase in Columbic repulsion, which can lead to smaller fibres. Optimization of process parameters for ternary system can even be challenging compared to binary systems.

The surface area of the electrospun filtration layer depends on the fibre diameter. Elements protruding from the nanofibre surfaces, such as salt crystals and nanowebs between electrospun fibres, may slightly increase the surface area and, thus, can have a positive effect on filtration efficiency. However, the major increased surface area can be achieved by introducing porosity into electrospun fibres. A uniform porous structure throughout the fibre can be achieved by electrospinning of self-organizing co-polymer to fibre web and then selectively removing one component from the structure. This was achieved using $\text{PS-}b\text{-P4VP(PDP)}_{1.0}$ system, which with removal of P4VP(PDP), led to porous PS fibres. The dimensions of the porous structure could be controlled by the choice of polymer blocks.

The strength of the thin nanofibre layer is limited. The breakage and the delamination of the nanofibre web from the substrate occurred in the case of our PA6 within an elongation range less than 30 %. The breaking method and the delamination tendency depend on the thickness of the web; whereas the thickest coating delaminated, the lighter coatings ruptured in many places and small pieces of coating remained on the textile surface. Due to the limited mechanical strength of the electrospun nanofibre web, the composite structure

can be made. The effective nanofibre filtration layer should be prepared onto relatively stiff supporting material such as nonwoven fabric, which can act as a coarse filter.

The filtration efficiency and the pressure drop of the composite filter material depend on the amount of nanofibres as well as the porosities of the nanofibre and the substrate web. Filtration efficiency increases with the increasing amount of nanofibres, and so does the pressure drop. The filtration efficiency of larger particles increases faster than that of smaller particles. The increase of pressure drop, on the other hand, may exhibit nearly linear growth. In the case of PA66 the filtration efficiency clearly increased even with a very low amount of nanofibres, which did not affect the pressure drop. Filtration efficiency of 0.5 g/m² coating was 95 % or above regardless of particle size, and with particle size of 0.73 µm the efficiency was over 99 %. Further increase of nanofibres above the coating weight of 0.5 g/m² was not found to have any benefit, but rather increased the pressure drop to an unusable range.

The multi-nozzle design needed for the production of larger webs can be practically constructed using nozzle tubes. Multiple nozzle tubes are used in order to obtain full coverage and even coating onto substrate. The modelling of the electric field revealed that while the voltage affected the strength of the field, the overall nature and shape of the field is mainly dependent on the distance between the nozzles and the collector. A stable process can be obtained in a multi-nozzle arrangement. In stable condition the sizes of the solution droplets at the tops of the nozzles are fixed in size, which enables the formation of the fibres with small diameter distribution. The stability of the spinning process is important since problems seem accumulate. When the flow of the solution is matched with the fibre formation speed, dripping of the solution is prevented. The dripping of the solution may cause damage to the newly formed nanofibre layer, and also promote the blocking tendency of the nozzles, which could cause unevenness to the nanofibre layer. With careful selection of the polymer and the values of the process parameters, the multi-nozzle design seems feasible method for continuous, large scale production of nanofibre layers for use in materials for filtration applications.

Thus, the following have been demonstrated. Nanostructured fibrous webs can be produced with the electrospinning method from polymeric and composite solutions. Such fibrous webs can be used as an effective layer in composite air filtration media. The preparation of the effective layer of such filtration media can be conducted as a continuous process suitable for commercialization.

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Summaries of Papers

Paper I

Ruotsalainen T., Turku J., Heikkilä P., Ruokolainen J., Nykänen A., Laitinen T., Torkkeli M., Serimaa R., ten Brinke G., Harlin A., Ikkala O.

Towards Internal Structuring: Electrospun Nanofibers by Self-Assembly of Polymeric Comb-Shaped Supramolecules

Advanced Materials, 17(8)2005, 1048-1052

<http://www3.interscience.wiley.com/journal/110438504/abstract>

Paper I examines the preparation of the electrospun nanofibres with the internal nanostructure obtained using self-organizing polymers. Electrospun fibres were formed from PS-*b*-P4VP block-co-polymer with PDP amphiphile, a system capable of hierarchical lamellar-within-spherical structured self-assembly. Structures with different length scales were analysed using different methods: AFM for the external structure of the electrospun fibres, TEM for the internal structure of the electrospun fibres and SAXS for the chemical structure of the block-co-polymer. It was shown that the relatively weak hydrogen bonded supramolecular structures survived the electrospinning process and self-assembled structures were obtained within the fibres, although the order of the structure was relatively low compared to the bulk. The properties of the porous structure could be affected by varying the block structure of the co-polymer. Nanofibres with mesoporous PS structure were obtained by removing P4VP(PDP) domains from the electrospun structure.

Paper II

Ristolainen N., Heikkilä P., Harlin A., Seppälä J.

Polyvinyl Alcohol and Polyamide-66 Nanocomposites Prepared by Electrospinning

Macromolecular Materials and Engineering, 291(2)2006, 114-122

<http://www3.interscience.wiley.com/journal/112234375/abstract>

Paper II studies the preparation of the electrospun composite fibres containing nano-sized clay as filler. Nanocomposite fibres of PVA and PA66 with MMT were prepared by electrospinning. Solutions for electrospinning were prepared using a mixing method involving different feeding orders of the components and using premixed composite prepared with *in-situ* polymerization in the presence of MMT. Increment of filler, incorporation of functional groups on polymer, and surface modification of MMT affected the molecular interactions within the solution and, thus, influenced the viscosity and electrospinnability of the solutions. The fibre structure and the size distribution of the filler particles were observed with SEM imaging, and the elemental analysis showed that filler was dispersed through the fibre network. The solution preparation order affected the size of the clay particles within the fibre. PA66-based nanocomposites exhibited a large enough

coating area on the substrate for measurements of contact angles and the time required for water penetration. Contact angles and the time required for water penetration were increased for most of the PA/nanoclay composites relative to the uncoated substrate.

Paper III

Heikkilä P., Sipilä A., Peltola M., Taipale A., Harlin A.

Electrospun PA Coating on Textile Surfaces

Textile Research Journal, 77(11)2007, 864-870

<http://trj.sagepub.com/cgi/content/abstract/77/11/864>

Paper III examines the preparation of electrospun coating onto the textile surfaces and considers the use of these structures in filtration. The electrospun coatings of PA66 nanofibres ranging from 0.02 g/m² to 0.5 g/m² were prepared onto different fibrous substrates including nonwoven, woven and knitted fabrics. Electrospun PA fibres had an average diameter of 140 nm with a standard deviation of 30 nm, and the thicknesses of the coating layers varied from 0.5 µm to 13 µm. Suitability of the PA nanofibre coating for filtering applications was evaluated on the basis of filtration efficiency and strain capacity determinations. Filtration efficiency clearly increased even with the lowest amount of nanofibres compared to uncoated samples, and with the highest nanofibre coating weight the filtration efficiency of sub-micron aerosol particles was over 90 %. The elongation capacity of the PA nanofibre layer was found to be insufficient for use with elastic materials. It was concluded that the nanofibre layer was suitable for the filtration application when used with a relatively rigid substrate such as spunbonded nonwoven, and preferably protected with cover layer because the nanofibre layer also delaminates easily from the textile surfaces.

Paper IV

Heikkilä P., Uusimäki J., Söderlund L., Kettunen L., Harlin A.

Exploitation of Electric Field in Controlling of Nanofibre Spinning Process

Polymer Engineering & Science, 47(12)2007, 2065-2074

<http://www3.interscience.wiley.com/journal/116837531/abstract>

Paper IV describes the modelling of the electric field of the electrospinning process. The electric field was modelled in order to determine the influence of two of the main process parameters, voltage and distance, on the electric field. Special interest was focused on the individual directional field components. The models of the electric field were compared with the experimental data and the observations collected from the electrospinning trials with PVA. The voltage had an influence on the strength of the field and also on the individual field components, but it did not have an effect on the shape of the electric field. The distance between the electrodes, on the other hand, determined the overall nature of the electric field since this, in addition to field strength, also affected the shape of the electric field. The smallest fibre diameters were

observed with the most intensive electric fields which can be obtained with the short distances. Long distances, on the other hand, were advantageous when targeting even coating because of the more homogenous electric field. The model of the electric field explained many phenomena in electrospinning, for example, the fibre quantity variation in the circular regions, but did not provide an exclusive control tool for the process.

Paper V

Heikkilä P., Taipale A., Lehtimäki M., Harlin A.

Electrospinning of Polyamides with Different Chain Compositions for Filtration Application

Polymer Engineering & Science, 48(6)2008, 1168-1176

<http://www3.interscience.wiley.com/journal/118860294/abstract>

Paper V presents the results of the several electrospinning trials made with different polyamides. Electrospun fibres were characterized with regard to their use in air filtration. In addition to common lower polyamides, PA6 and PA66, also higher polyamides with higher lengths of diacid and diamine segments PA612, PA614, PA1012 and PA1014 were included in this study. To the best of our knowledge they were now electrospun for the first time. Longer non-polar chain segments of the higher polyamides could, in theory, indicate higher dielectricity compared to PA6 and PA66, which would be an advantage in filtration applications. The solubility in the polar formic acid and the electrospinnability of the higher polyamides were impaired with the increased length of the chain segments. Sub-micron fibres were obtained with all polyamides even though PA614, PA1012 and PA1014 solutions needed heating for electrospinning. The fibre diameters of PA66 and PA612 were smaller and fibre production rates higher than those of other polyamides. PA66 was our best choice, and PA612 and PA6 our second options for commercial filtration applications in terms of their electrospinnability, production rate, fibre diameter and diameter distribution. Filtration efficiency measurements were conducted with PA66 coated nonwoven samples, and the efficiencies of more than 95 % of the particles having diameter of 0.16 μm and above was achieved with 0.5 g/m² coating of PA66 nanofibres. Above that coating weight the nanofibre layer mainly increased the pressure drop to an unusable range without a significant further improvement in filtration efficiency.

Paper VI

Heikkilä P., Harlin A.

Parameter Study of Electrospinning of Polyamide-6

European Polymer Journal, doi:10.1016/j.eurpolymj.2008.06.032

<http://www.sciencedirect.com/science/journal/00143057>

Paper VI studies the effects of several solution and process parameters on the properties of the electrospun fibres and the electrospinning process. The study was performed for process and operation analysis using

continuous electrospinning equipment consisting of multiple nozzles and utilizing the orthogonal experimental design. The parameters chosen for this study were the polymer grade, the viscosity and the salt content of the solution, the solvent grade, the voltage, the distance, the nozzle size and the feeding pressure of the solution. The effect of the parameters on the fibre diameters and the electrospinning process were observed and the results were compared with the literature. The viscosity and the salt content of the solution and the strength of the electric field were the main parameters determining the fibre diameters. The main parameter affecting productivity was the strength of the electric field and, thus, the voltage and the distance. Literature findings on the influences of certain variables are often contradictory and unexpected and our results were no exception. We observed concave dependency curves between several parameter and measured properties. This kind of ambiguity may be caused by two different phenomena having opposing effects on the properties of the electrospun fibres. Increase in conductivity of the solution and in the field strength, for example, can both have two reverse effects: firstly, an increase in the flow rate, which can lead to larger fibres, and secondly an increase in Columbic repulsion, which can lead to smaller fibres. Different polymer-solvent systems may act differently, and also the effect of parameters may vary depending on variation range as well as the level of other parameters. Since the interactions between the parameters and the cumulative effects of the parallel and reverse factors can be misleading, it was concluded that with most of the parameters there are no universally applicable laws of electrospinning.